

**THERMODYNAMIC AND KINETIC STUDIES ON THE SYSTEM
Zr (or Hf) Cl₄—ALKALICHLORIDE AND FABRICATION OF A
REACTOR FOR FRACTIONAL SUBLIMATION OF
Na₂ZrCl₆ AND Na₂HfCl₆**

By
GANTA SATYANARAYANA REDDY



**DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
SEPTEMBER, 1976**

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A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

* 3 *

By
GANTA SATYANARAYANA REDDY

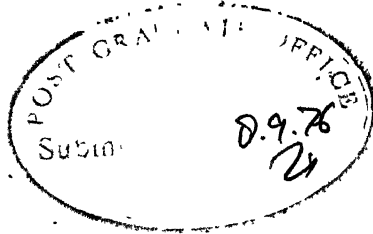
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CERTIFICATE

Certified that this work on '(a) Thermodynamic and Kinetic Studies on the Zr (or Hf)Cl₄-Alkalichloride System and (b) Fabrication of a Reactor for Fractional Sublimation of Na₂ZrCl₆ and Na₂HfCl₆' has been carried out under my supervision by Mr. Ganta Satyanarayana Reddy and that it has not been submitted elsewhere for a degree.

Dated: September, 1976

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POST GRADUATE OFFICE
This thesis has been approved
for the award of a Degree of
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LIST OF SYMBOLS

C	Concentration ^{δC} reagent
D	Diffusion coefficient, mm ² /hr.
d ₀	Size of the (sodiumchloride) particle, mm
F	Fraction reacted
ΔH_R^0	Heat for decomposition of the reaction, K Cal/mole
j =	$K_j \cdot t$, from Jander's equation (18)
K _{EQ}	Equilibrium constant
K'	Reaction rate constant, (15 th equation), mm ² /hr.
K'	From equation 25, mm ^{3/2} /g ^{1/2}
K _j	Specific rate constant due to Jander's equation, hr ⁻¹
K _{cv}	Specific rate constant due to Carter-Valensi equation, hr ⁻¹
K	Master constant, mm ² /hr.
M _r	Molecular weight of solid reactant
MCl	Alkalimetal chloride, where M = potassium, rubidium or cesium
P _{ZrCl₄}	Partial pressure of zirconium tetrachloride, mm of Hg.
P	Total pressure, atmosphere
r ₀	Initial radius of the particle (or sphere), mm
T	Temperature, °K
t	Time, hours

XCl_4	Tetrachloride, where X = zirconium or hafnium
y	Thickness of the product layer, mm
z	Swelling parameter = $\frac{\text{Volume of solid reaction product}}{\text{Volume of solid reactant product}}$
ρ_r	Density of the solid reactant, g/cm ³
α_1	Stoichiometry factor

ABSTRACT

Some thermodynamic and kinetic studies on the system Zr (or Hf)Cl₄-alkalichlorides are reported in this thesis. Thesis also describes the reactor that has been fabricated to achieve fractional sublimation of hexachloro compounds for separation of zirconium and hafnium.

Fractional sublimation of the hexachloro compounds exploit the difference in their stabilities. The stability of any of these compounds is defined by the pressure of zirconium (or hafnium) tetrachloride over them. Accordingly vapour pressure measurements have been done over the compounds, K₂ZrCl₆, K₂HfCl₆, Rb₂ZrCl₆, Rb₂HfCl₆, Cs₂ZrCl₆, Cs₂HfCl₆.

A transpiration techniques has been employed to measure the rates of reaction of ZrCl₄ with packed beds of sodiumchloride of various particles sizes to obtain the kinetic data for initial stages of reaction. Such data are needed to determine the working conditions of the reactor employed in fractional sublimation.

CHAPTER - 1

INTRODUCTION

1.1 General Introduction

Zirconium alloys are becoming increasingly important for nuclear reactors for a unique combination of properties. They have the requisite combination of physical and mechanical properties even at high temperatures and very good corrosion resistance in most coolants. In addition, they are weldable and workable. Above all they are noted for the low resistance they offer to the passage of thermal neutrons generated in the fission reactions. It is known that the construction material used for making the core and cladding must have 'low neutron absorption cross-section' to facilitate the propagation of the chain reaction.

Table 1, gives the values of thermal neutron absorption cross-section for some elements. It indicates that there are four metals with relatively low values. These are; beryllium, magnesium, aluminium and zirconium. The use of the alloys of the first three elements in nuclear reactors is limited mainly for their lower melting points.

Naturally occurring zirconium ores always contain about one-half to several per cent of hafnium. Because of

Table I Thermal-neutron absorption cross-section of elements used as core construction materials (Hafnium as a control rod material)

Element	Absorption cross-section, (barns)*	Melting point (°C)
Beryllium	0.010	1280
Magnesium	0.063	651
Zirconium	0.180	1845
Aluminium	0.230	660
Niobium	1.1	2415
Iron	2.53	1539
Molybdenum	2.5	2625
Copper	3.69	1083
Nickel	4.6	1455
Titanium	5.8	1725
Hafnium	105	2222

Reference: S.M. Shellon, Metallurgy of Zirconium (Book), McGraw Hill publication.

* Barn is unit area for nuclear cross-section

$$1 \text{ Barn} = 10^{-24} \text{ cm}^2.$$

the chemical similarity of zirconium and hafnium it is very difficult to remove hafnium to produce pure zirconium. Yet, it is absolutely necessary to reduce hafnium to less than 200 ppm to produce zirconium of the nuclear grade. This is so because even the presence of small amounts of hafnium drastically increases the absorption of neutrons in zirconium alloys because of the high value of neutron absorption cross-section of hafnium (see Table 1).

The extraction of zirconium, therefore, involves a purification stage aimed mainly at almost complete removal of hafnium. The various processes for hafnium removal have been reviewed in the literature¹ and will not be discussed here. The methods fall mainly into two categories, the physical methods and the chemical methods. The former includes processes such as solvent extraction, fractional crystallisation, etc. These physical methods have been more successful and, therefore, been the basis of industrial processes so far. Chemical methods involving chemical reactions (usually of various halides) have not yet been successfully exploited for the production of nuclear grade zirconium.

The present studies report further progress in a programme of investigations concerning a chemical method of separating zirconium and hafnium. The method, to be reviewed

subsequently in detail, depends on reactions of zirconium and hafnium tetrachlorides with alkali halides. The present work has the following aims:

a) Measurement of vapour pressure over the hexachloro compounds [potassium hexachloro zirconate (K_2ZrCl_6), Rubidium hexachloro zirconate (Rb_2ZrCl_6), Cesium hexachloro zirconate (Cs_2ZrCl_6) and potassium hexachloro hafnate (K_2HfCl_6), Rubidium hexachloro hafnate (Rb_2HfCl_6), Cesium hexachloro hafnate (Cs_2HfCl_6)]. Reliable vapour pressure for these systems would establish the relative stabilities of hexachloro compounds. It is generally known that the hafnate of any alkalichloride is more stable than the zirconate. This difference in stabilities may be exploited for the separation of zirconium from hafnium through a process of fractional sublimation as discussed earlier by Bhat².

b) Measurement of the rate of the reaction of a packed bed of sodium chloride particles with a flowing stream of tetrachloride gas Any fractional sublimation technique would involve counter-current flow of gas and solids and a continuous gas, solid reaction. Kinetic data, therefore, are needed for reactor design and all calculations of separation efficiency.

c) Reactor design The thesis describes a reactor which has been designed and fabricated for carrying out the fractional sublimation of hexachloro compounds of zirconium and hafnium for the separation of the two elements.

1.2 General Description of the System $\text{Zr (or Hf)Cl}_4\text{-MCl}$, Where M is an Alkali Metal

This system is of potentially great importance for the development of a pyrometallurgical separation of zirconium from hafnium and, accordingly several thermodynamic and kinetic studies on this system have been reported recently³⁻⁷. The following is a brief summary of the earlier investigations carried out in this laboratory.

Majumdar and Ray^{1,8} have investigated a new method for the separation of hafnium from zirconium. The method involved continuous reaction between gaseous mixture of ZrCl_4 and HfCl_4 and solid sodiumchloride in a packed bed flow reactor. The experimental data indicated that hafnium tetrachloride in the gas phase reacts to form solid hexachloro hafnate in preference to the corresponding zirconium compound. The influence of a number of parameters e.g., temperature, flow rate, particle size and bed length has been studied. The decrease in flow rate and particle size, and increase in bed length were found to favour separation,

while temperature had only little effect. In a number of runs separation coefficients greater than that predicted by thermodynamic calculations were achieved.

Mazurkar et al^{3-5,9-11} have investigated, by gravimetry, the kinetics of the reaction of vapours of ZrCl_4 and HfCl_4 separately and as well as their gaseous mixtures with solid sodium chloride spheres leading to the formation of sodium hexachloro zirconate (Na_2ZrCl_6), hafnate (Na_2HfCl_6) and $\text{Na}_2\text{Zr}(\text{Hf})\text{Cl}_6$ respectively, in a closed system. The course of the reaction was followed by measuring the change in weight of the reacting sodium chloride spheres by calibrated quartz springs. Inert marker experiments were also conducted to augment the formulation of reaction mechanisms. The rate of formation of the compounds were studied as a function of tetrachloride pressure, temperature and sphere size. Under identical conditions the reaction with HfCl_4 was invariably found to be slower. In all their cases the reaction occurred at a sharp interface. Accordingly, the kinetic data were tested against various appropriate heterogeneous solid-gas kinetic models. Of these models only the Carter-Valansi product phase transport controlled model gave consistently good fit. The empirical relations representing the effects of various reaction parameters are as follows:

Effect of pressure, P: $K_{cv} \propto P^{1/n}$ (1)

where $n = 1.98$ for $ZrCl_4$ reaction, in the range 257 to 1013 mm, Hg at 450°C

$n = 2.13$ for $HfCl_4$ reaction in the range 367 to 945 mm, Hg and at 450°C

Effect of sphere size, R_o : $K_{cv} \propto \frac{1}{R_o^m}$ (2)

where $m = 1.92$ for $ZrCl_4$ reaction at 450°C and 745 mm, Hg pressure

$m = 2.12$ for $HfCl_4$ reaction at 450°C and 945 mm, Hg pressure

The apparent activation energies for the formation of the two hexachloro compounds are:

Formation of Na_2ZrCl_6 : 7.5 K.cal/mole at 745 mm, Hg pressure in the range of 425-500°C

Formation of Na_2HfCl_6 : 13 K.cal/mole at 945 mm, Hg pressure and in the range of 440-484°C

The possible reaction mechanisms have been postulated in the light of the pressure and temperature dependence of the specific rate constant and the marker experiments. On the basis of the experimental evidence, the transport of

the chlorine ions from the unreacted core towards the outer product-gas interface appeared to be the most likely reaction mechanism. The material transport presumably occurred by a vacancy mechanism. In the range of the experimental conditions employed in the investigations, the formation of both hexachloro zirconate and hexachloro hafnate conforms to the same reaction mechanism. However, there were indications to suggest that the reaction mechanism undergoes a change with change in the polymorphic form of the reaction product.

Some preliminary investigations on simultaneous formation of the hexachloro compounds were also carried out by reacting sodium chloride spheres with vapour mixtures of zirconium tetrachloride and hafnium tetrachloride. In these investigations, additional experiments were performed to ascertain the partial pressure of the reacting gas mixture, the composition of the gas phase. The total pressures were determined by separate experiments.

Roy¹² has designed and fabricated an apparatus for kinetic studies by the transpiration technique. He has investigated the kinetics of the reaction ZrCl_4 vapours with particles of NaCl, KCl and mixtures of these. It was shown that the reaction with pure KCl was faster than that with pure NaCl. However, much higher rates of reaction were obtained with some intermediate mixture compositions.

Bhat² has measured the vapour pressures over ZrCl_4 , HfCl_4 , Na_2ZrCl_6 and Na_2HfCl_6 compounds. He has also done kinetic studies on the system Zr (or Hf) Cl_4 - NaCl and or KCl using the transpiration technique and substantiated the earlier findings of Roy¹². He has made theoretical calculations for fractional decomposition and sublimation of the compounds Na_2ZrCl_6 and Na_2HfCl_6 . The calculations were done for different gas flow rates, different initial compositions of the vapour and for different final compositions of the vapour. It was shown that increase in solid flow rate and decrease in gas flow rate decreases the number of plates necessary to achieve any predetermined separation.

The investigations¹³ in this area carried out by other laboratories have been reviewed by Bhat².

1.3 The Present Report

The present report has three main sections in accordance with the three main aims of the investigation mentioned earlier. Chapter 2 deals with the techniques of vapour pressure measurements, the experimental arrangement employed in the present work and a discussion of the experimental results.

Chapter 3 describes the experimental set-up for measurement of the rate of the gas-solid reaction between

packed beds of sodium chloride particles and flowing zirconium tetrachloride vapours and reports kinetic data for different particle sizes at a fixed temperature and partial pressure of zirconium tetrachloride. It also includes a discussion of the data in the light of established theories on gas-solid reactions of this type. An attempt has been made to examine the relationship of the kinetic data for such systems with these for single pellet experiments.

Chapter 4 gives the engineering description of a reactor which has been designed and fabricated in the laboratory. The reactor is an inclined kiln with a rotating screw conveyor and various inlets and outlets. It has been designed to achieve a pyrometallurgical separation of zirconium and hafnium through fractional sublimation.

Chapter 5 summarises the main conclusions of the present investigations and lists some suggestions for future work. The thesis is concluded by a list of references.

CHAPTER - 2

VAPOUR PRESSURE MEASUREMENTS

2.1 Introduction

There are several established methods for measuring vapour pressures over volatile compounds. Generally these techniques are of specific applicability in given pressure ranges. Some of the main techniques which have been used for compounds similar to those investigated in the present work are reviewed here.

2.2 Vapour Pressure Measurement Techniques

2.2.1 Vapour pressure measurement using quartz Bourdon spiral

This apparatus for measuring the equilibrium vapour pressures is shown in Figure 1. Used by Sadoway and Flengas¹⁴, it consisted of a Bourdon type fused quartz spiral. The spiral was enclosed in a quartz chamber in such a way that the salt vapour from the sample entered only the inside of the spiral while air could be admitted to the chamber surrounding the spiral to equilibrate pressures inside and outside the spiral. The gauge served only as a null point detector while the equilibration pressure was read directly on a closed-end mercury manometer.

It has been claimed that, because of the compact size, the spiral needs only a very minute amount of vapour for deflections and, therefore, it can be used for very small sample sizes. It is also said to be able to withstand large and sudden pressure changes. However, it is cumbersome to use and needs extreme care in handling. Moreover, there may be some hysteresis in the deflection of the spiral.

2.2.2. Vapour pressure measurement using spoon gauge

The spoon gauge has been used in many vapour pressure measurements. For example Lister and Flengas¹⁵ have used for measuring vapour pressures over several alkali and alkaline earth hexachloro compounds of zirconium and hafnium. The apparatus incorporating the spoon gauge is shown in Figure 2. In this set-up the spoon gauge replaces the Bourdon quartz spiral. While acting as the null point detector, it separates the mercury in the manometer from the tetrachloride vapours. To allow for the evacuation of the system a by-pass of the spoon gauge is provided which is later sealed under vacuum.

The main drawback of the spoon gauge lies in its very sensitivity. It is easily broken by sudden pressure changes or too much pressure difference. The gauge if made properly, however, can measure pressure with great accuracy.

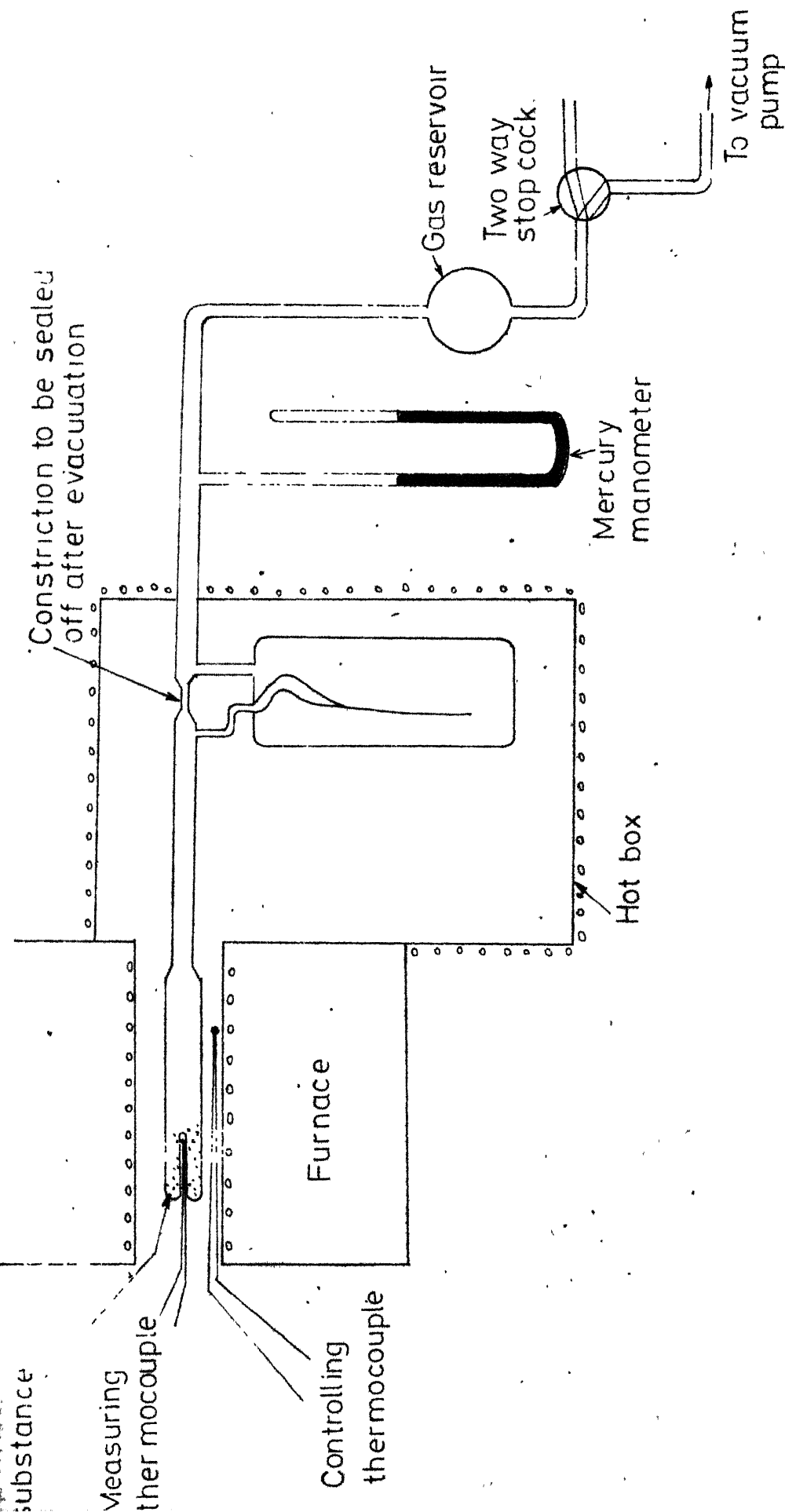


FIG. 2 APPARATUS FOR VAPOUR PRESSURE MEASUREMENT USING SPOON GAUGE

2.2.3 Vapour pressure measurement using transpiration technique

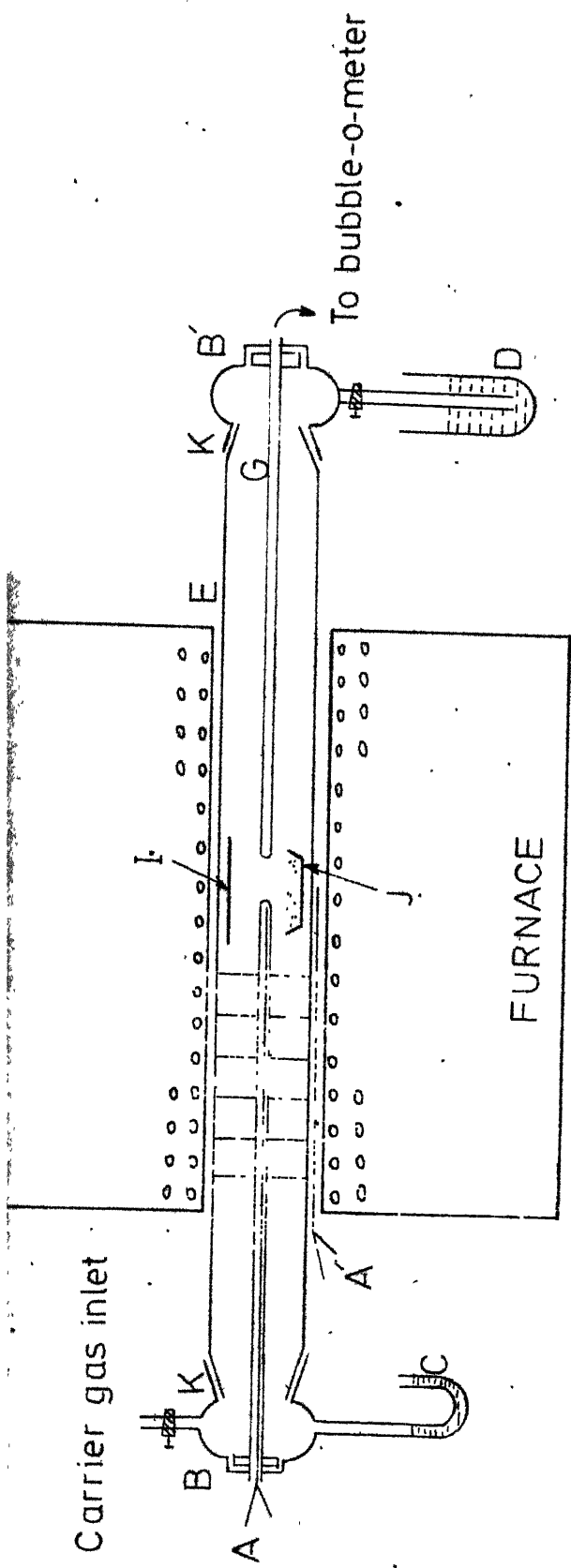
Transpiration techniques are generally used for measuring relatively higher vapour pressures. For example, Garg and Bhatt¹⁶ have used this technique for the measurement of vapour pressures in the ZrCl_4 -NaCl system. The apparatus is shown in Figure 3. The special features of the apparatus are the small inlet and outlet tubes which are reduced to diameters of about 0.85 mm to minimize diffusion of ZrCl_4 in either direction.

The flow rate of the carrier gas is maintained constant throughout the run and the quantity of ZrCl_4 deposited in the condenser is determined by direct weighing. The partial pressure of ZrCl_4 is obtained by using the well-known relation

$$P_{\text{ZrCl}_4} = \frac{n_1}{n_1 + n_2} P \quad (3)$$

where n_1 and n_2 are the moles of ZrCl_4 and argon passed in a given duration and 'P' is the total pressure (normally 1 atm.).

The technique is not applicable if the flow rate of the carrier gas is too low or too high. The satisfactory intermediate region of flow rate must be obtained first by preliminary measurements.



A-MEASURING THERMOCOUPLE

B-B'- VEECO SEAL

D - BY PASS BUBBLER

F- SILICA THERMOCOUPLE SHIELD

H - INCONEL RADIATION

J - SILICA BOAT

A'-CONTROLLER THERMOCOUPLE

C-TOTAL PRESSURE MANOMETER

E- SILICA TUBE

G-GLASS CONDENSER TUBE

I-INCONEL LINER

K- CONE SOCKET

FIG.3 SCHEMATIC DIAGRAM OF VAPOUR PRESSURE MEASURING APPARATUS (TRANSPORTATION METHOD)

The method suffers from the disadvantage that large amounts of the volatile compound must be available for transpiration. Moreover, the compound must have appreciable vapour pressures to saturate the carrier gas.

2.2.4 Vapour pressure measurement using volumetric pressure element

Kim and Spink¹⁷ have used this technique for measuring vapour pressure over some of the hexachloro compounds. Their apparatus is shown schematically in Figure 4 which is self explanatory. The volumetric pressure element (Figure 4c) consists of a stainless steel diaphragm and a liquid chamber. The element used by Kim and Spink was supplied by Taylor Instrument Co., Rochester, N.Y. (Model 103), and consisted of a diaphragm (0.005 in thick and 3.776 in diameter) welded in the vapour pressure element which did not permit the contact of reactive vapour with liquid NaK. NaK is a eutectic mixture of sodium and potassium metals which melts at -12.3°C and has low vapour pressures even at temperatures as high as 400°C . The gases generated by the volatile compounds exert a force on the diaphragm which in turn transfers the impulse to a pressure indicator through the liquid NaK filled capillary. Precision of the pressure is about $\pm 0.5\%$ of the indicated values and the pressure on the indicator were read within ± 5 mm, of Hg accuracy.

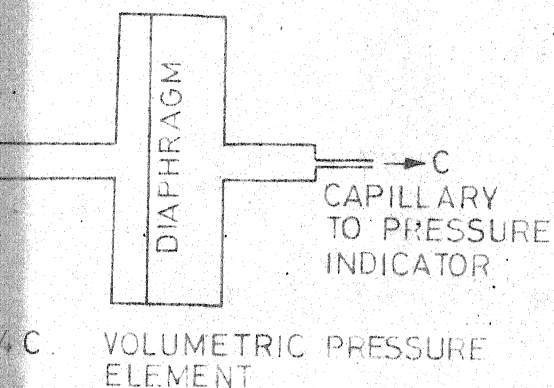
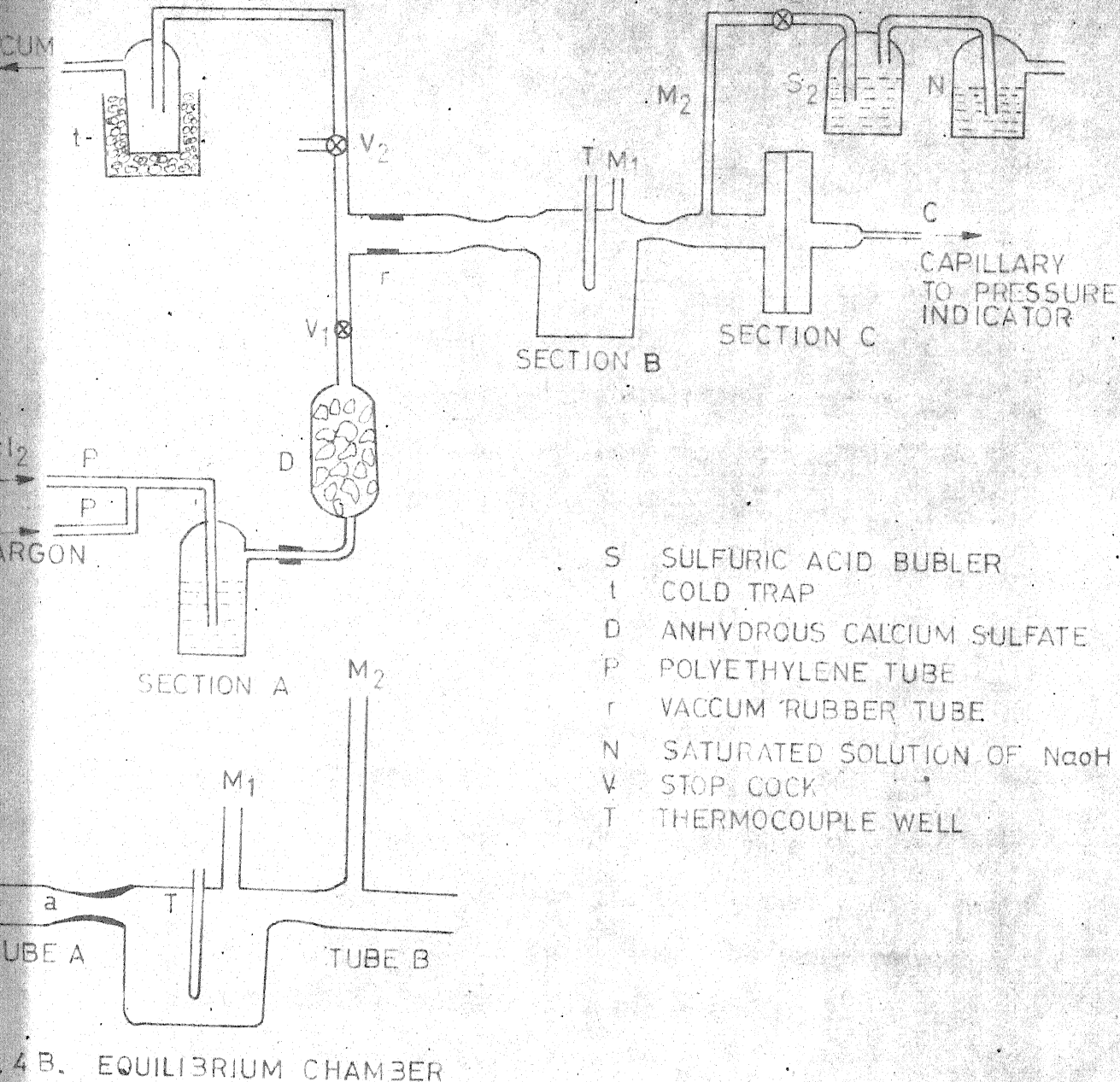


FIGURE 4. SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

The experimental procedure of Kim and Spink was as follows. The pyrex equilibrium chamber was first thoroughly cleaned, washed and dried. A weighed amount of metal (Zr or Hf) was placed in tube 'A' at a section about 3 in. from point 'a'. A weighed amount of dry salt (NaCl/KCl) was placed in the equilibrium chamber through tube M_1 , then the ' M_1 ' was closed by flame. The apparatus was repeatedly evacuated and argon gas admitted until it dried. Then argon gas was allowed to flow at a rate of 100 to 200 cc/minute.. The chlorine flow rate was regulated next for chlorination at 300 to 350°C. After complete conversion, argon and chlorine gas flow was stopped. Then the tube ' M_2 ' was closed off by fusing. The equilibrium chamber was evacuated and closed off by fusion at point 'a'. The temperature of the equilibrium chamber was then increased gradually and the vapour pressure was read directly.

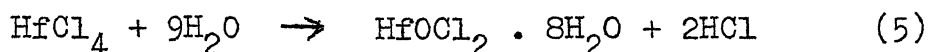
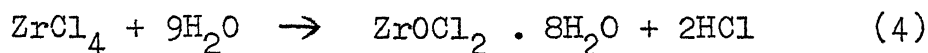
2.3 The Experimental Technique and Procedure for the Measurement of Vapour Pressures in the Present Work

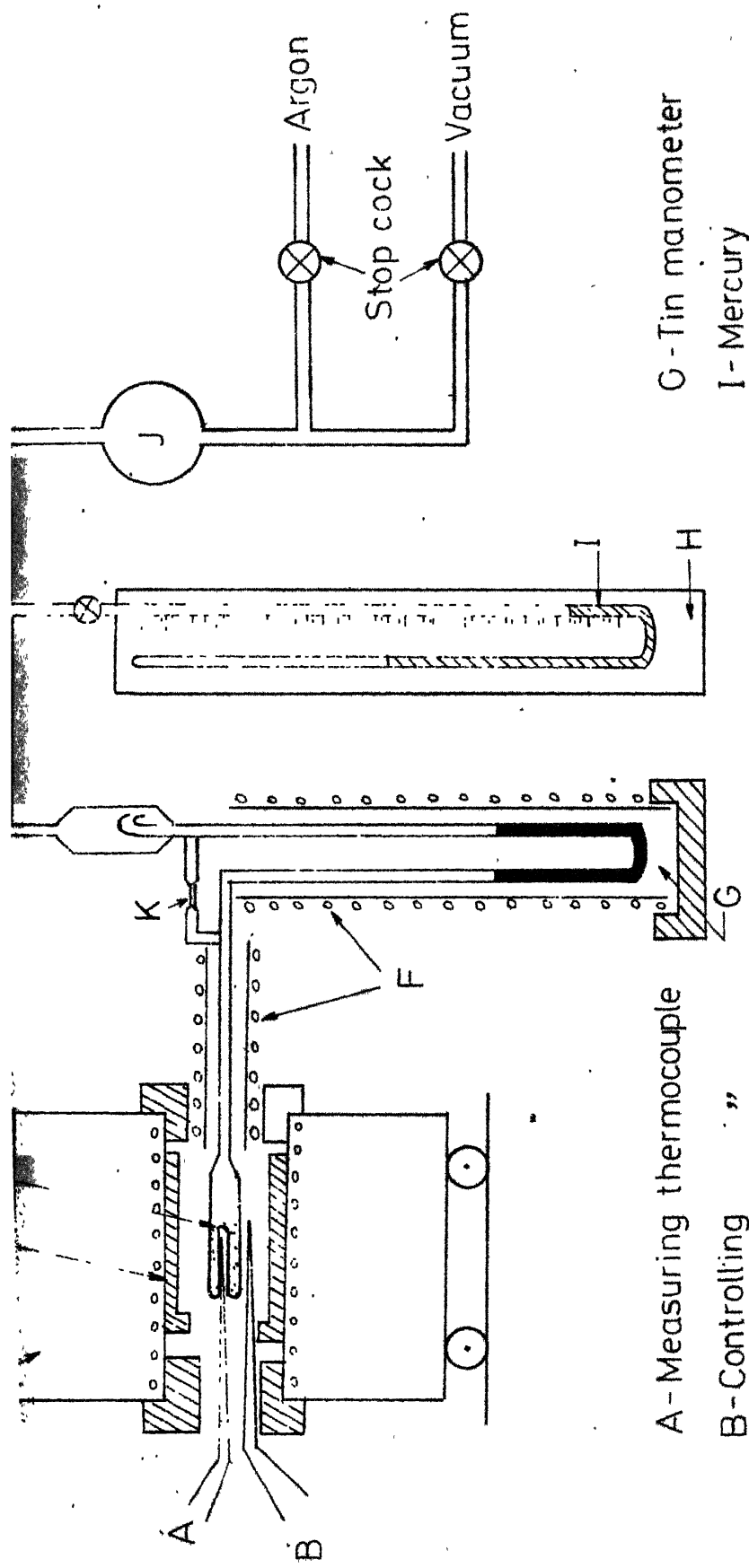
In the present work, vapour pressure over the compounds e.g., K_2ZrCl_6 , Rb_2ZrCl_6 , Cs_2ZrCl_6 and K_2HfCl_6 , Rb_2HfCl_6 , Cs_2HfCl_6 have been measured by a static method employing a simple isoteniscope of molten tin.

The molten tin isoteniscope has been widely used earlier for measuring vapour pressures over alkali hexachloro compounds^{18,2}. The apparatus used is shown in Figure 5. The set-up consisted of a quartz glass bulb containing the sample, a quartz U-trap and a mercury manometer. The sample temperature was controlled and measured using a special furnace to within $\pm 1^\circ\text{C}$ and a chromel-alumel thermocouple. The thermocouple had been calibrated against a certified platinum - 13% rhodium vs. platinum standard. The liquid tin isoteniscope was connected to a closed-end mercury manometer, a gas reservoir and vacuum/argon leads as shown. This arrangement allowed application of an opposing gas pressure for equilibration of the levels in the two arms of the tin manometer.

2.4 Materials

During the course of these experiments the importance of purity was of major consideration. Zirconium (or hafnium) tetrachloride is subject to rapid and irreversible hydrolysis by atmospheric water vapour according to the following reactions:





- A - Measuring thermocouple
- B - Controlling "
- C - Trolley furnace
- D - Aluminium block
- E - Glass bulb containing the compound
- F - Tube furnaces

- G - Tin manometer
- I - Mercury
- H - Graduated scale
- J - Gas reservoir
- K - Square connection

FIG.5 APPARATUS FOR MEASUREMENT OF VAPOUR PRESSURE BY MOLTEN TIN ISOTENISCOPE

Therefore, all operations involving HfCl_4 , ZrCl_4 and the chloro compounds were conducted either in argon filled dry box or in sealed glass tubes and bulbs. The alkali chlorides were also handled with similar care.

2.4.1 Preparation of the tetrachlorides

The nuclear grade zirconium tetrachloride used in this work was supplied by Nuclear Fuel Complex, Hyderabad. Hafnium tetrachloride used, however, was produced from pure oxides obtained from Bhabha Atomic Research Centre, Trombay. Zirconium content of the HfO_2 was about 5 per cent. Tetrachlorides of both zirconium and hafnium were purified before use by vacuum distillation.

Hafnium tetrachloride was produced by reduction-chlorination of the oxide using carbon as the reducing agent. Chlorination was carried out by passing anhydrous chlorine through a packed bed of oxide pellets kept in a furnace at 700°C . The pellet mixture contained about 15 per cent carbon, 4 per cent dextrine (binder), 3 per cent water and rest hafnium oxide. A sketch of the apparatus is shown in Figure 6. The experimental procedure was as follows. The entire set-up was flushed with argon for about 3-4 hours to remove traces of moisture present in the apparatus and the pellets. Then chlorine gas was admitted after moisture

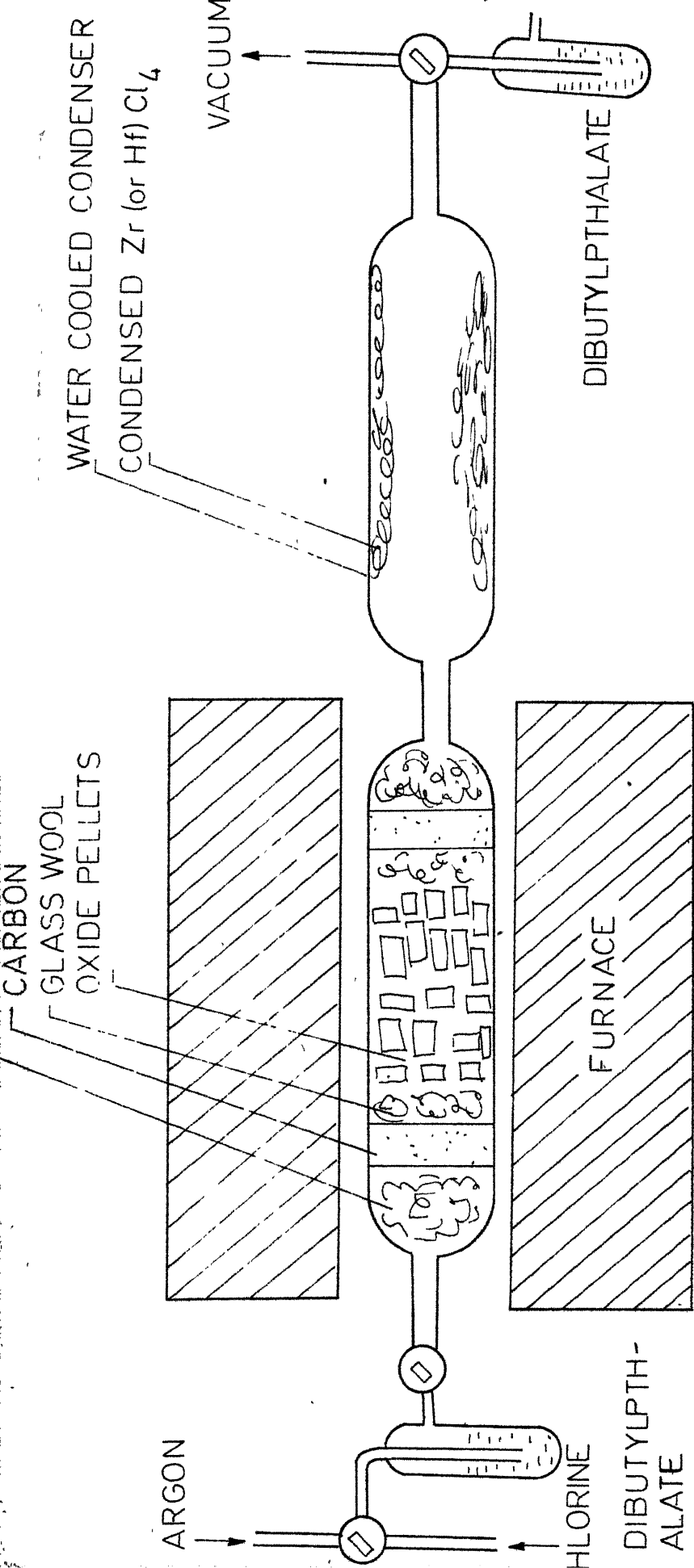


FIG 6 EXPERIMENTAL SETUP FOR THE REDUCTION-CHLORINATION OF ZIRCONIUM OR HAFNIUM OXIDE

elimination. The tetrachloride vapours produced along with the oxides of carbon and unreacted chlorine were led to a water cooled condenser. The uncondensed gases were allowed to escape through bubbler containing dibutylphthalate. After sufficient tetrachloride had been collected, the condenser was detached from the rest of the apparatus by fusing the inlet and outlet constrictions by hand torch under vacuum. Then the sealed tetrachloride pyrex tube was broken at one end and the tetrachloride was transferred into a distillation apparatus in the argon filled dry box.

2.4.2 Distillation of tetrachlorides

The distillation was performed in a horizontal 35 mm x 60 mm pyrex tube closed at one end. A schematic figure of the apparatus is shown in Figure 7.

The tetrachloride was transferred into the pyrex tube in the argon filled dry box and covered with a thick layer of glass-wool which had been washed with alcohol and dried at 170°C for 25 hours. Next some copper turnings, cleaned in 10 per cent hydrochloric acid, rinsed with distilled water and dried in the oven for about 1-2 hours, was placed in the tube. Some more glass wool was placed upon the copper turnings. The tube was closed by a rubber stopper with an inlet connected to a cold trap and to a vacuum pump.

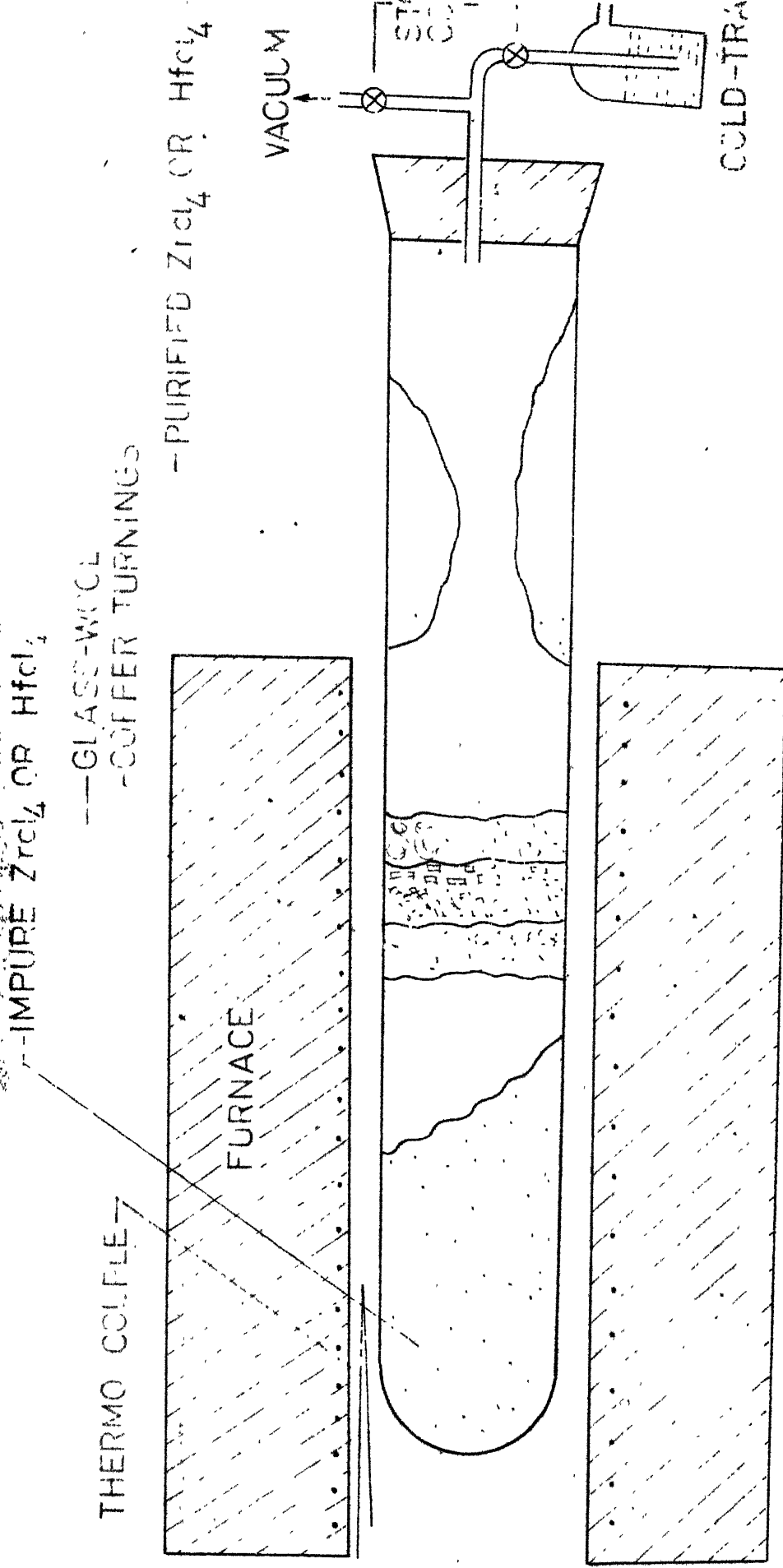


FIGURE 7. DISTILLATION APPARATUS FOR PURIFICATION OF ZIRCONIUM TETRACHLORIDE OR HAFNIUM TETRACHLORIDE

The tube was then placed in a horizontal furnace and heated to about 160°C under vacuum for about 4-5 hours to remove the absorbed gases, mainly hydrochloric acid gas.

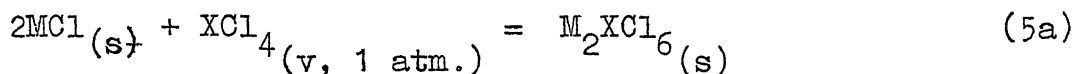
The temperature was then raised slowly to 350°C, kept steady for 3-4 hours. The tetrachloride sublimed and vapour condensed in the cooler parts of the tube. After cooling, the sublimation tube was stoppered by and transferred into the dry box again where the tetrachloride was transferred into air-tight containers.

2.4.3 Preparation of alkali hexachloro compound

Several workers such as Morozov and Sun-In-Chzhu¹⁹, have prepared the hexachloro salts by direct reaction of stoichiometric amounts of the tetrachloride and the alkali chloride in sealed glass bulbs. This method, however, suffers from three disadvantages. First, it is important that the tetrachlorides be freshly distilled and handled on absolutely dry atmosphere to prevent the addition of hydrolysis products, HfOCl_2 , to the reaction mixture. Secondly, it is impossible to ascertain whether or not all the materials have in fact reacted. That is, the stoichiometry of the compound is not definitely known. Thirdly, to achieve completion of the reaction, the alkalichloride (NaCl , KCl , RbCl , CsCl) should be present as a liquid,

otherwise the reaction with solid powders is rather slow since it is controlled by diffusion. In addition, at such high temperatures, the high pressures of the tetrachloride (ZrCl_4 or HfCl_4) would exceed the endurance of the reaction quartz tubes. For example, at 641°C the vapour pressure of solid HfCl_4 is 1400 atm.¹⁸

The method applied in the present work was similar to that reported by Asvestas¹⁸. A known amount of alkali-chloride ~~was~~ reacted with an excess of purified tetrachloride vapour at 1 atm. pressure to form the stoichiometric compound M_2XCl_6 or a mixture of MCl and M_2XCl_6 determined from the weight gain of the MCl . The reaction



where $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$

$\text{X} = \text{Zr or Hf}$

was carried out in a sealed pyrex tube, as shown in Figure 8. By weighing the MCl salt before and after the reaction, the stoichiometry of the product can be accurately determined. The solid mixture ~~was~~ ground and reacted repeatedly ~~until the~~ reaction is almost complete. This method is particularly well suited for the study of new compounds where the stoichiometry has not been previously determined.

TEMPERATURE OF TETRACHLORIDE = 350°C

TEMPERATURE OF ALKALI CHLORIDE = ~~450°C~~ 450°C

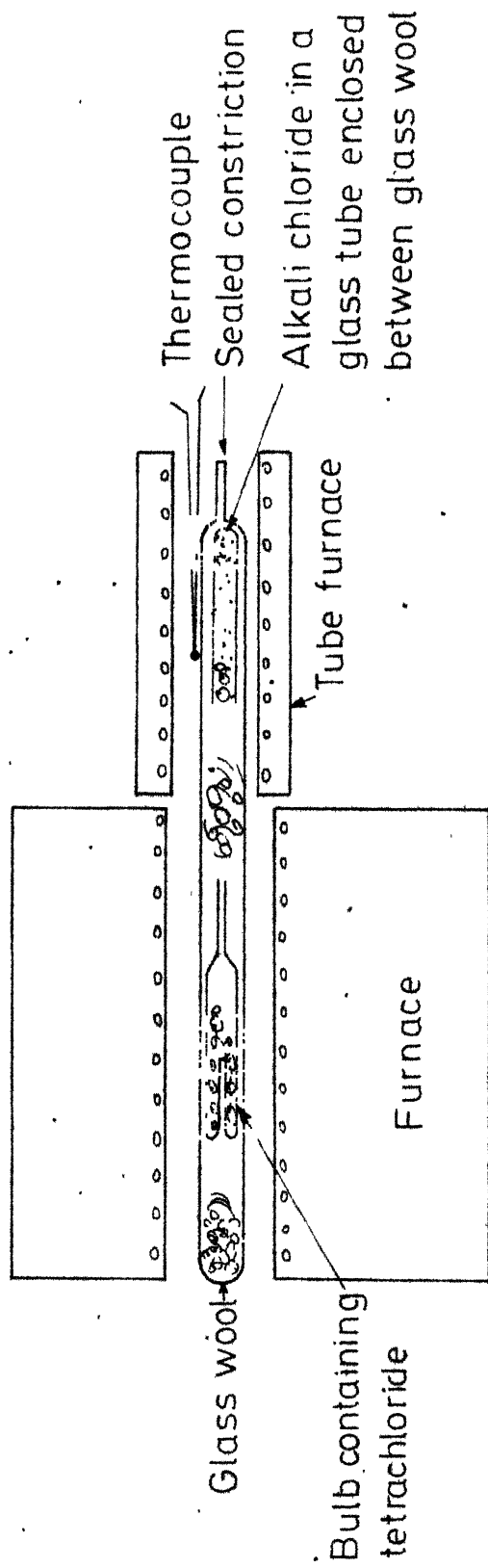


FIG.8 APPARATUS FOR PREPARATION OF HEXACHLOROCOMPOUNDS

The exact technique is described below and the experimental apparatus is shown in Figure 8.

The tetrachloride was transferred to a pyrex glass bulb while the alkalichloride, accurately weighed was transferred to a pyrex glass tube of diameter 16 mm and length 130 mm in the argon filled dry box. The bulb and the tube were loaded into a reaction (pyrex) tube (diameter = 28 mm length = 500 mm). The glass reducer was then joined to reaction tube. Then the reaction tube was loaded into the furnace where it was gradually heated till 170°C under vacuum for about 3 to $3\frac{1}{2}$ hours. Then the constriction provided in the reaction tube was next fused by a hand torch. Now the reaction tube was loaded into the two horizontal furnaces such that the alkalichloride portion of the tube rests in one furnace while the tetrachloride portion rests in the other furnace. Slowly the chloride furnace was heated to 450°C , while the tetrachloride furnace was heated very slowly until 340°C . After about 6 hours the reaction tube was rotated to allow mixing of the alkalichloride. The reaction was carried out for about 4 more hours. Then the reaction tube was brought down to room temperature and transferred to the argon filled dry box where the seal was broken. And the reacted MCl was weighed, mixed thoroughly and transferred into another reaction tube along with the fresh XCl_4

in the bulb. This procedure repeated until the reaction was nearly complete. Finally the product i.e., M_2XCl_6 was transferred to a vycor glass bulb in the dry box and stoppered. The compound M_2XCl_6 was then ready for the measurement of vapour pressure.

2.4.4 Experimental procedure for measuring vapour pressure using molten tin isoteniscope

The experimental set-up is shown in Figure 5. The U-trap was first filled with small vacuum purified tin chips. Next a quartz bulb of standard dimensions was filled with the appropriate compound in the dry box and stoppered. The bulb was joined to the U-trap quickly after removing the stopper and the whole system was evacuated. The total time from stopper removal to establishment of a fair vacuum was around one minute. The bulb was then heated slowly to about $240^{\circ}C$ to remove gases and simultaneously the tin chips were also melted to form a null point detector. The vacuum degassing of the entire system was continued for at least 16 hours and then the constriction at the bridge connecting the two arms of the 'U' was fused by a hand torch. The system was then ready for pressure measurements. Vapour pressures were measured by fixing the temperature, levelling the isoteniscope and then reading off the mercury manometer. The purpose of the gas reservoir was to reduce sudden

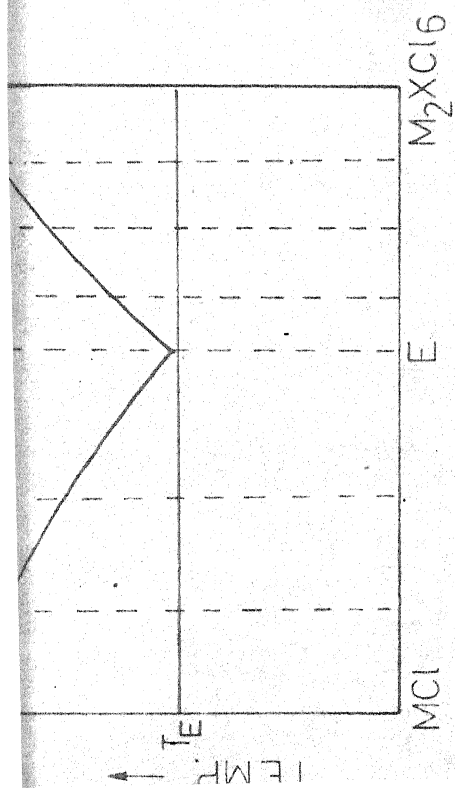
surges in pressure which might throw the tin out of the U-trap. A special feed-back device was incorporated in the mercury manometer side to prevent ejection of tin due to uncompensated pressure rise in the bulb.

It may be mentioned that the presence of tin in the system does not introduce any error. By extrapolation of the data of Ruff and Bergdahl²¹ the pressure of tin at these temperatures were calculated by Dutrizac¹³ to be less than 10^{-5} torr. Moreover, it has been conclusively shown that the reaction between the tetrachlorides and molten tin are negligible²².

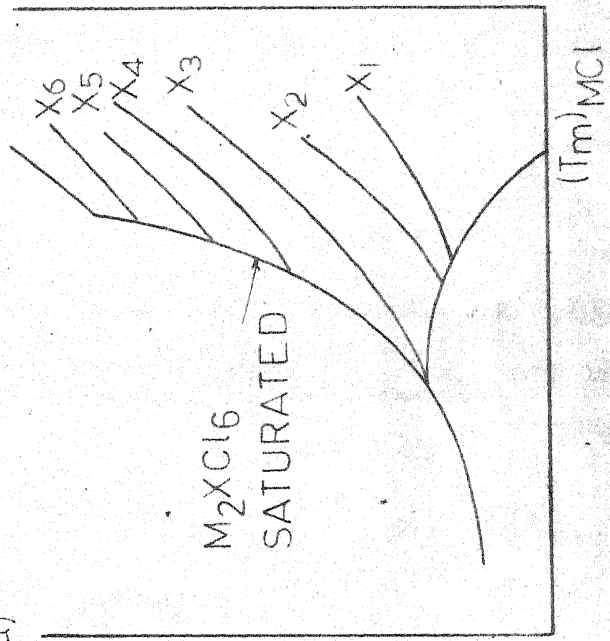
2.5 Theoretical Background

2.5.1 Thermodynamic relationships in reactive Zr (or Hf)Cl₄-alkali-hexachloro compound systems

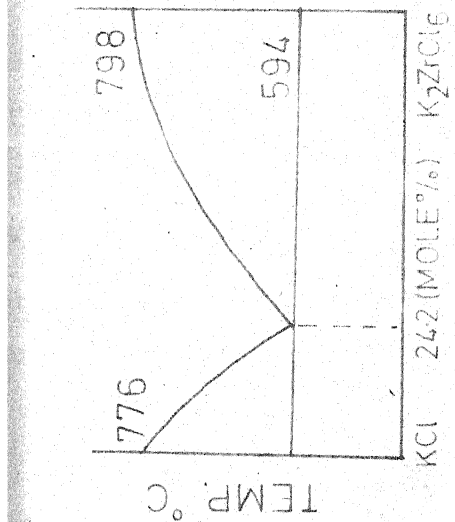
A typical phase diagram representing the $MCl-XCl_4$ system is depicted ^{elsewhere} ~~in Figure 10~~. In our present work only the sub-system $MCl-M_2XCl_6$ is of interest. ^{Fig 10.} The predicted shape of the pressure-temperature curves for various selected compositions in this subsystem are shown in Figure 10(b). The correspondence between these diagrams and the $MCl-M_2XCl_6$ subsystem is obtained from the following considerations.



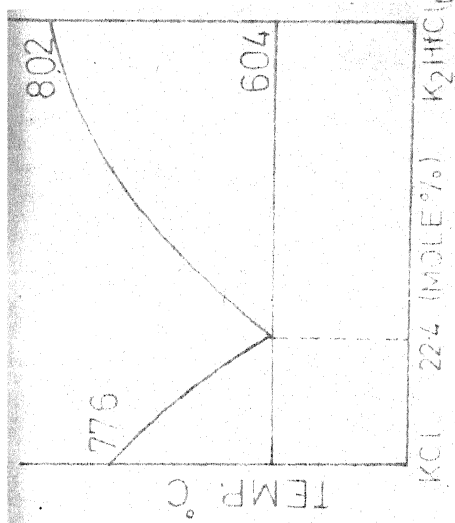
(a)



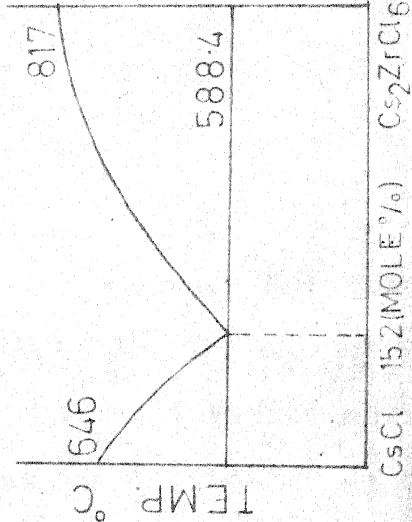
(b)



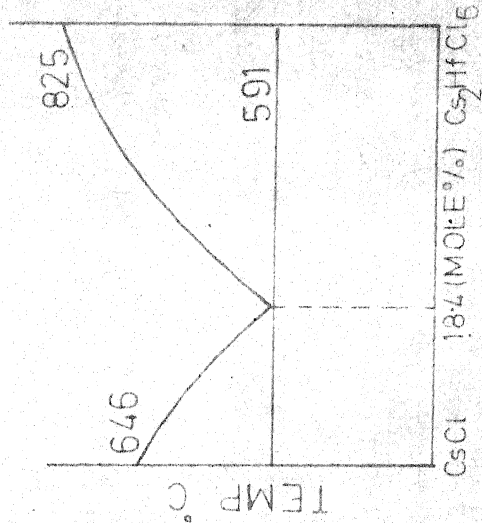
$K_2ZrCl_6 \rightarrow$



$K_2HfCl_6 \rightarrow$



$Cs_2ZrCl_6 \rightarrow$

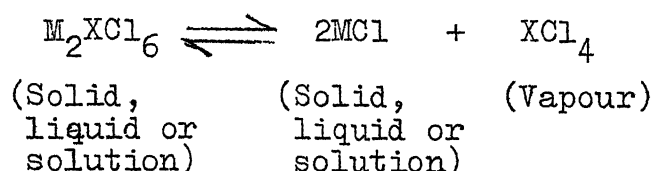


$Cs_2HfCl_6 \rightarrow$

G10 PREDICTED PRESSURE VS TEMPERATURE CURVES FOR A SYSTEM HAVING ONE REACTIVE COMPONENT

FIG.11 SCHEMATIC PHASE DIAGRAMS (FROM THE LITERATURE^{15,20})

In the subsystem $\text{MCl}-\text{M}_2\text{XCl}_6$, the equilibrium pressure of XCl_4 vapour is determined by the reaction:



The equilibrium constant can be written as:

$$K_{\text{EQ}} = \frac{a_{\text{MCl}}^2 \cdot f_{\text{XCl}_4}}{a_{\text{M}_2\text{XCl}_6}} \quad (6)$$

where a_{MCl} and $a_{\text{M}_2\text{XCl}_6}$ are the activities of MCl and M_2XCl_6 , respectively, and f_{XCl_4} is the fugacity of XCl_4 vapour. At low pressures and high temperatures the fugacity may be taken as being equal to the pressure of the tetrachloride vapour. The states of unit activity for the condensed phases are selected as the pure solids at all temperatures. For the vapour the standard state is chosen as the metal tetrachloride vapour at 1 atmosphere pressure.

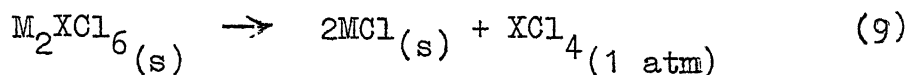
At temperatures below the temperature of the eutectic T_{E_1} , the phases present are the pure solids MCl and M_2XCl_6 , and XCl_4 vapour. Because of the choice of standard states in this range the activities of a_{MCl} and $a_{\text{M}_2\text{XCl}_6}$ are unity. Thus:

$$P_{\text{XCl}_4} = K_{\text{EQ}} \quad (7)$$

The variation of the equilibrium pressure with temperature is given by the Van't Hoff relationship:

$$\frac{d \ln P_{\text{XCl}_4}}{d(1/T)} = - \frac{\Delta H_R^0}{R} \quad (8)$$

That is, over a limited temperature range the plot of $\log P_{\text{XCl}_4}$ versus $(1/T)^\circ\text{K}$ should be linear of slope $-\Delta H_R^0/R$. ΔH_R^0 is the heat for the decomposition reaction with the reactants and products in their standard states. The standard state reaction is:



Therefore, the pressure exerted over the system corresponds to the decomposition of the pure solid M_2XCl_6 . Pressure measurements in this region are independent of mixture composition, and all vapour pressures over various compositions should be represented by a single curve. Equation (7) is only valid in the case of negligible or no solid solubility of the pure materials.

The second region of interest includes all compositions on the M_2XCl_6 side of the eutectic, defined by the corresponding eutectic temperature T_{E_1} and the liquidus line. In this region the solutions of MCl and M_2XCl_6 are saturated with respect to M_2XCl_6 solid.

Accordingly, $a_{M_2XCl_6(\text{solution})} = 1$

and thus:
$$P_{XCl_4} = \frac{K_{EQ}}{a_{MCl}^2} \quad (10)$$

From equation (10) it may be predicted that the temperature-pressure curve will change slope at the eutectic temperature, since as the temperature is increased beyond this point the activity of MCl becomes less than unity. Thus the pressure of the vapour would be expected to increase as shown.

In the range between the eutectic and the liquidus temperatures for a given mixture, the compositions of the solutions in equilibrium with the pure solid changes following the liquid solubility line. Thus the activity of MCl will be changing continuously because of temperature and composition changes. At any specific temperature in this range the pressure of XCl_4 exerted by any two mixtures of initially different composition will be identical upto the temperature of the lower melting mixture. The liquidus solubility line will, therefore, be represented by a common pressure curve.

For a given mixture, when the temperature is increased beyond the corresponding liquidus temperature,

the system will be described by a homogeneous solution of MCl and M_2XCl_6 , and by XCl_4 vapour. The equilibrium pressure is now given by:

$$P_{\text{XCl}_4} = K_{\text{EQ}} \cdot a_{\text{M}_2\text{XCl}_6} / a_{\text{MCl}}^2 \quad (11)$$

Once having crossed the temperature of the liquid solubility line the pressure curve will undergo a decrease of slope because of the introduction of the activity of M_2XCl_6 (equation (11)) which is less than unity. This is illustrated by curves 3, 4, 5 and 6 in Figure 10(b), each corresponding to a different mixture.

Differentiating the free energy equation with respect to temperature and combining with the Gibbs-Helmholtz it can readily be seen that

$$\frac{d \ln P_{\text{XCl}_4}}{d(1/T)} = \frac{\Delta H_R^0 - (\overline{\Delta H}_{\text{M}_2\text{XCl}_6} + 2\overline{\Delta H}_{\text{MCl}})}{R} \quad (12)$$

Therefore the plot of $\log P_{\text{XCl}_4}$, versus $(1/T)^\circ\text{K}$ will again become linear over a limited temperature range provided the terms within the brackets in the right hand side are small compared to ΔH_R^0 , otherwise the line would be a curve.

Considering compositions in the MCl saturated side of the eutectic at $T_L > T > T_{E_1}$, where T_L is the liquidus temperature, the phases present are pure solid MCl in equilibrium with a solution of M_2XCl_6 and MCl , and XCl_4 vapour.

In this range, as defined before,

$$a_{\text{MCl}_4} = 1$$

$$\text{and } P_{\text{XCl}_4} = K_{\text{EQ}} \cdot a_{\text{M}_2\text{XCl}_6} \quad (13)$$

For a given mixture, increasing the temperature to that above the eutectic would cause a decrease in slope of the pressure curve. The predicted shape of the common pressure curve representing the liquidus line in the phase diagram is again given in Figure 10(b). The pressure for the liquidus line for MCl decreases as the solutions become more dilute in M_2XCl_6 and eventually reaches zero at the melting point of pure MCl, as shown in Figure 10(b).

For temperatures higher than the liquidus temperatures, equation (11) again becomes applicable and the pressure curves for various compositions slope upwards at the corresponding liquidus temperatures as shown by curves 1, 2 and 3 in Figure 10(b).

The compounds investigated in the present work are the hexachloro compounds with 2-6% alkali chlorides. The vapour pressure data, therefore, may be analyzed in terms of a composition line very close to that for the pure compound in the subsystem $\text{MCl-M}_2\text{XCl}_6$.

2.5.2 Phase diagrams in the systems alkalichloride- zirconium (or hafnium) tetrachloride

The available information on the phase diagrams in these systems is summarised schematically in Figure 11. The question marks and dotted lines indicate the absence of information and shows only the expected trends. The vapour pressure data obtained in the present investigation would be examined in relation to these diagrams. As mentioned earlier the data are concerned exclusively with almost pure hexachloro compounds with small amounts of the respective alkalichlorides. The thermodynamic information on the pure compounds, as available in the literature is summarised in Table 2. It should be noted that there is discrepancy amongst various workers. Many data are questionable in themselves. For example, the vapour pressure data of Morozov and co-workers¹⁹ do not correspond with the vapour pressure equation given by the same workers. Previously the vapour pressures over sodium hexachloro zirconate and sodium hexachloro hafnate has been measured by Bhat². These compounds were better than 99 per cent pure. He has also measured the pressures over the pure tetrachlorides. Two sets of his results are summarised in Figures 12 and 13. The data obtained by some other workers are also indicated. The good agreement of these data with those of the others and the nature of the

Table II Thermodynamic information on pure compounds from the literature

Compound	Melting point (°C)	Eutectic temperature (°C)	Decomposition temperature (°C)	Reference
K_2ZrCl_6	798 790±5 804	594 600±5 —	— — 831	(19) (30) (7)
K_2HfCl_6	802	604	—	(19)
Rb_2ZrCl_6	812	—	904	(7)
Cs_2ZrCl_6	805 817	572 588.4	— 1040	(19) (7)
Cs_2HfCl_6	825.5 820	591 590	947 —	(18) (19)
Na_2ZrCl_6	646 695 626±5	548 539 525±5	634 — —	(15) (31) (30)
Na_2HfCl_6	660 680±1	540 —	— —	(19) (7)

Compound	LiCl	NaCl	KCl	RbCl	CsCl
Melting point (°C)	613	801	776	715	646

Blank space indicate non-availability of information.

work

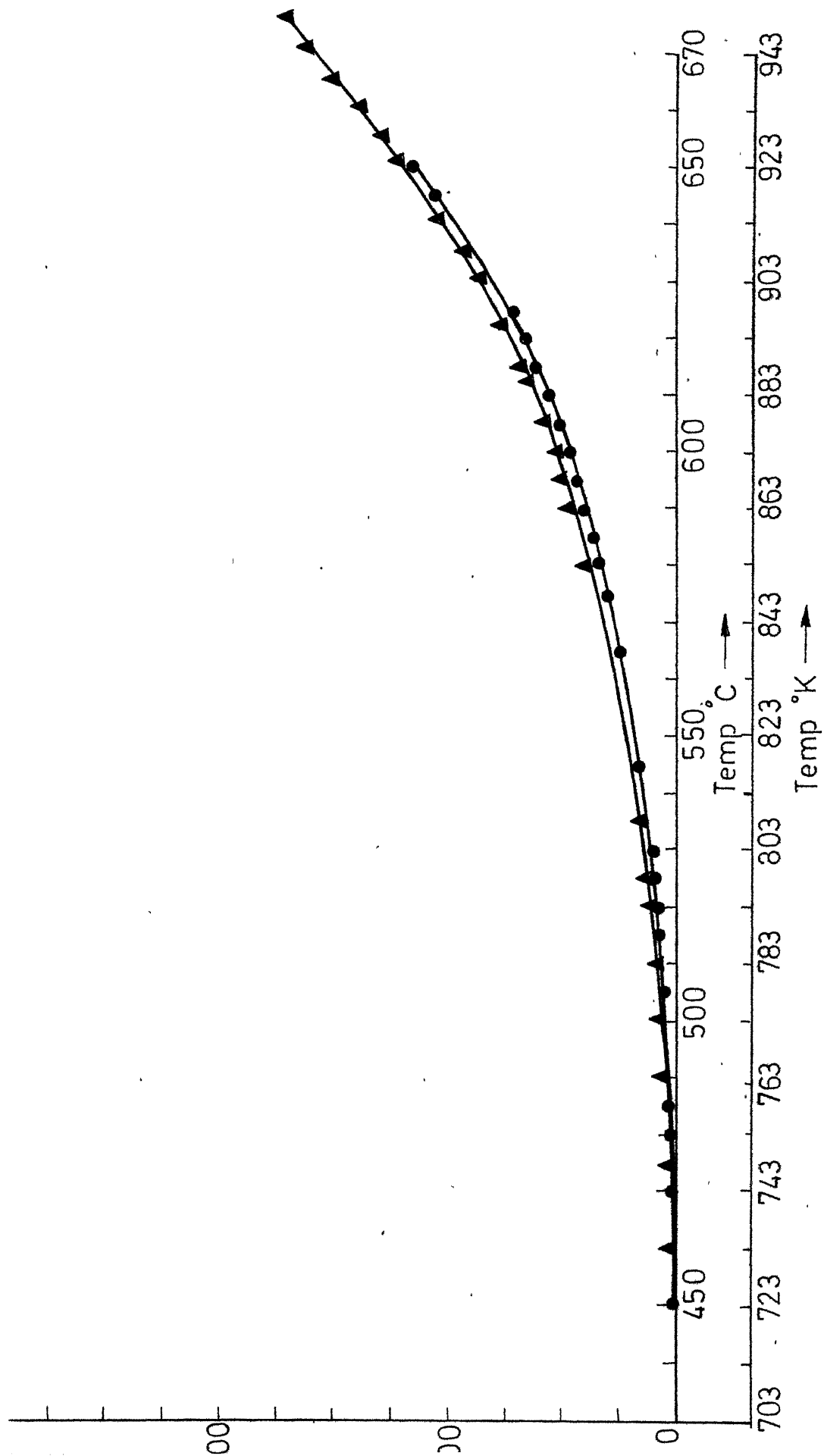
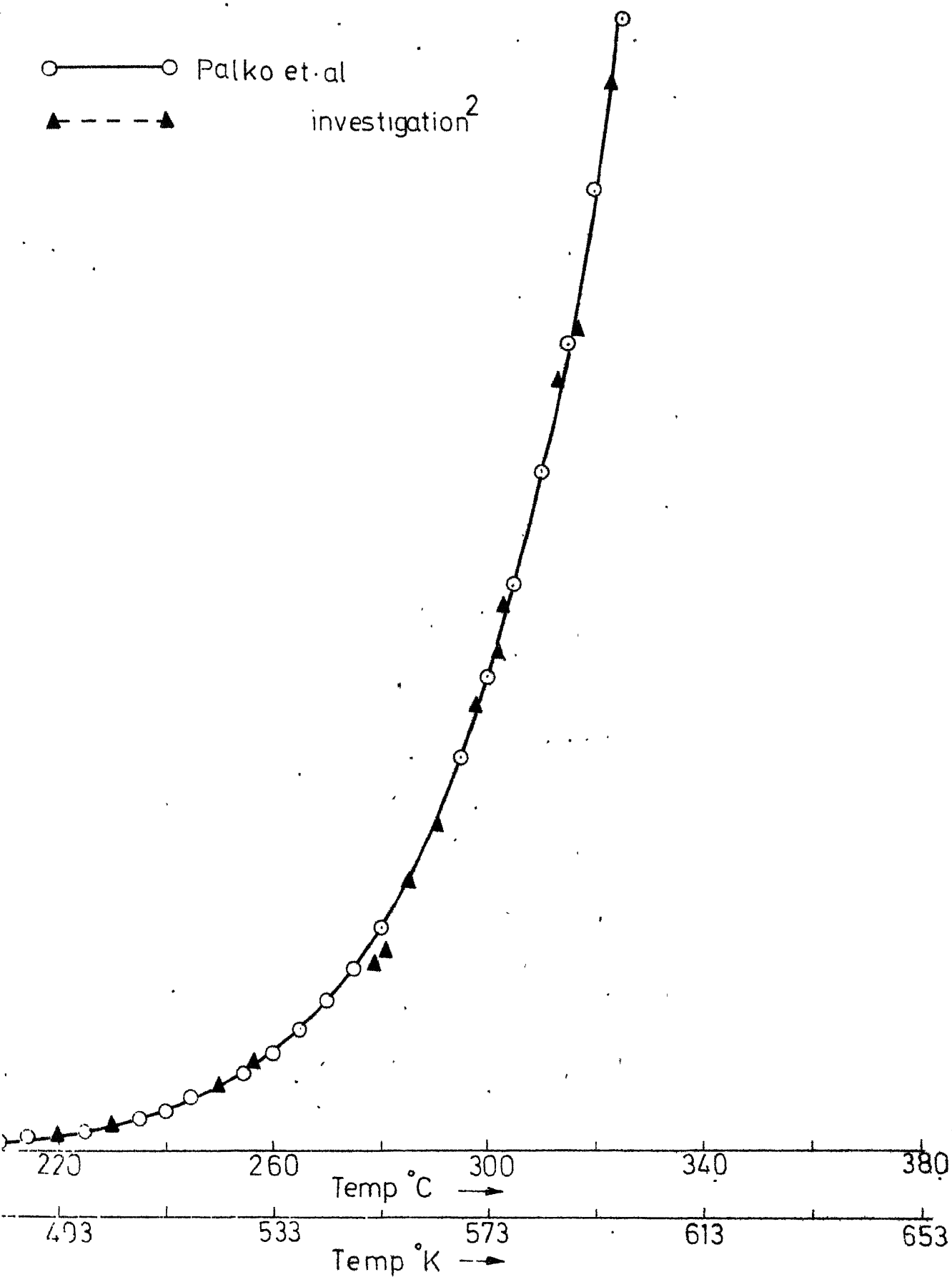


FIG 12 EFFECT OF TEMPERATURE ON VAPOUR PRESSURE OF Na_2HfCl_6



13 EFFECT OF TEMPERATURE ON VAPOUR PRESSURE OF HfCl_4

log P vs. $1/T$ plot indicate that his data reliable. The same apparatus has been used in the present investigation also. The equations for the vapour pressures as given by Bhat² are the following.

Na_2ZrCl_6	$\log P_{\text{ZrCl}_4} = - \frac{7965.9}{T} + 11.5071$	(438 - 646°C)
Na_2HfCl_6	$\log P_{\text{HfCl}_4} = - \frac{6188.7}{T} + 9.1116$	(452 - 660°C)
ZrCl_4	$\log P_{\text{ZrCl}_4} = - \frac{2553.6}{T} + 6.7983$	(210 - 381°C)
HfCl_4	$\log P_{\text{HfCl}_4} = - \frac{5116.4}{T} + 11.5715$	(190 - 323°C)

2.6 Results and Discussions of the Present Work

For brevity all vapour pressure data obtained in the present investigation are presented only as log P (torr) vs. $1/T$ plots. The actual values of pressure at various temperatures over any given compound are given in the Appendix I.

Figure 14 shows the vapour pressure over potassium hexachloro zirconate (K_2ZrCl_6). The figure shows the plot of the predicted shape with linear segments and abrupt changes of slope. The figure shows a well defined liquidus point of 736°C which is almost 60°C lower than that reported by Pint and Flengas.⁷ The vapour pressures measured are

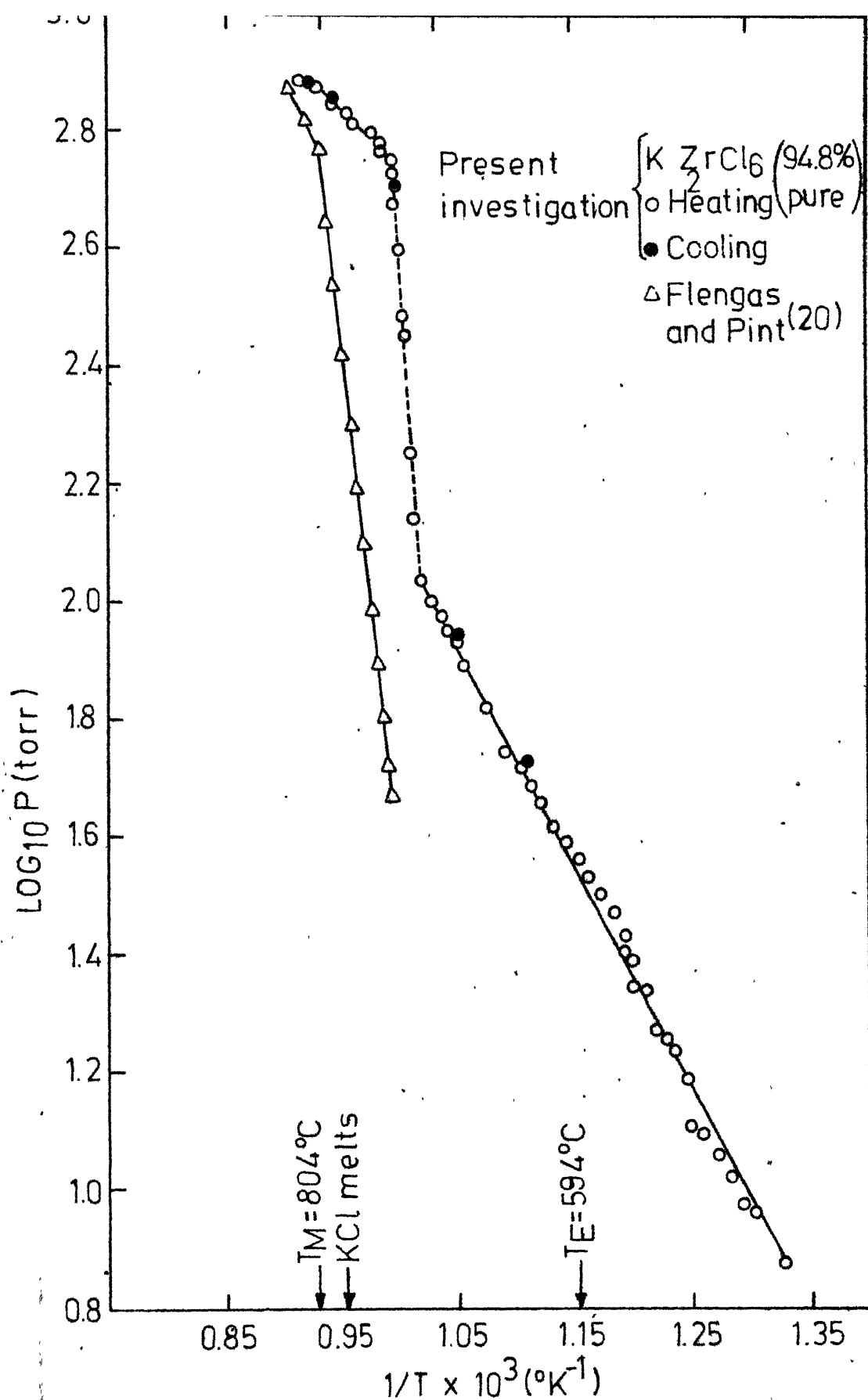
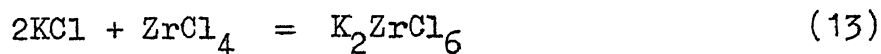


Fig.14 - Logarithmic vapor pressure of $ZrCl_4$ (torr) vs. $\frac{1}{T} (^\circ K^{-1})$ over K_2ZrCl_6 .

also higher. Moreover, the present data indicate a transformation at about 713°C.

Vertical arrows indicate the temperatures of melting of the hexachloro compounds, potassium chloride and the eutectic as reported in the literature. It should be noted that while heating a mixture of K_2ZrCl_6 and KCl some eutectic may form through the presence of intermediate gas/liquid phases at the interfaces. The system is not in equilibrium unless it forms the requisite amount of eutectic as required by the phase diagram. Because of the nonequilibrium situation the eutectic formation may be delayed or completely absent while heating. Therefore the pressure data obtained may or may not be identical with that for an absolutely pure compound. The trend in the data for higher temperatures accordingly are represented by the dotted line. The figure shows that, because of the KCl impurity an eutectic does form although the formation is delayed.

It should also be noted that the vapour pressure data will not be reproducible unless the compound is absolutely pure. Consider the reaction



$$K = \frac{a_{K_2ZrCl_6}}{P_{ZrCl_4} \cdot a_{KCl}^2} \quad (14)$$

Consider a mixture of K_2ZrCl_6 and small amounts of KCl. During heating both the solids are in the pure state and are, therefore, at unit activity. Hence P_{ZrCl_4} is uniquely defined by temperature alone. However, if there is melting of KCl and consequent mixing then a_{KCl} is no longer unity. Although $a_{K_2ZrCl_6}$ remains unity because the melt is saturated with the compound. The vapour pressure measured, therefore, will be more. This is consistent with the observations that the values measured during cooling are slightly higher.

Figure 15 shows the vapour pressure over the almost pure potassium hexachloro hafnate (K_2HfCl_6). The results show the expected change in the slope for liquidus transformation. Another transformation is also indicated at a lower temperature which may be due to eutectic formation. The results indicate pressures much higher than that reported by Morozov and Sun In-Chzhu¹⁹ earlier. The melting point and the liquidus point, however, are close. The figure also indicates the melting point of potassium chloride, potassium hexachloro hafnate and the eutectic as reported in the literature and shows that the eutectic formation, in this case, takes place at almost the eutectic temperature.

Figure 16 shows the vapour pressure over rubidium hexachloro zirconate (Rb_2ZrCl_6). This curve also shows the

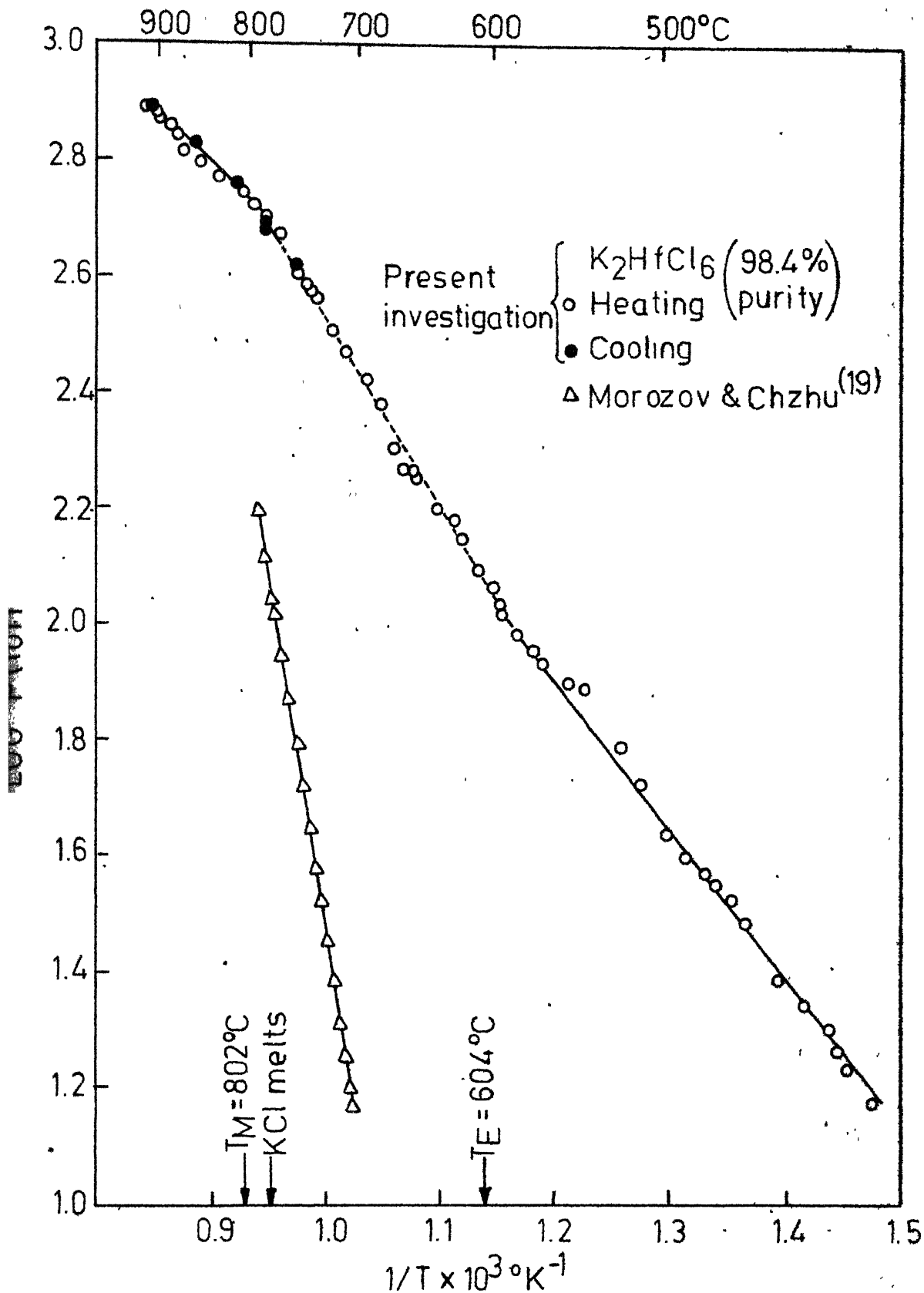


Fig.15 - Logarithmic vapor pressure of HfCl_4 (torr) vs. $1/T$ ($^\circ\text{K}^{-1}$) over K_2HfCl_6 .

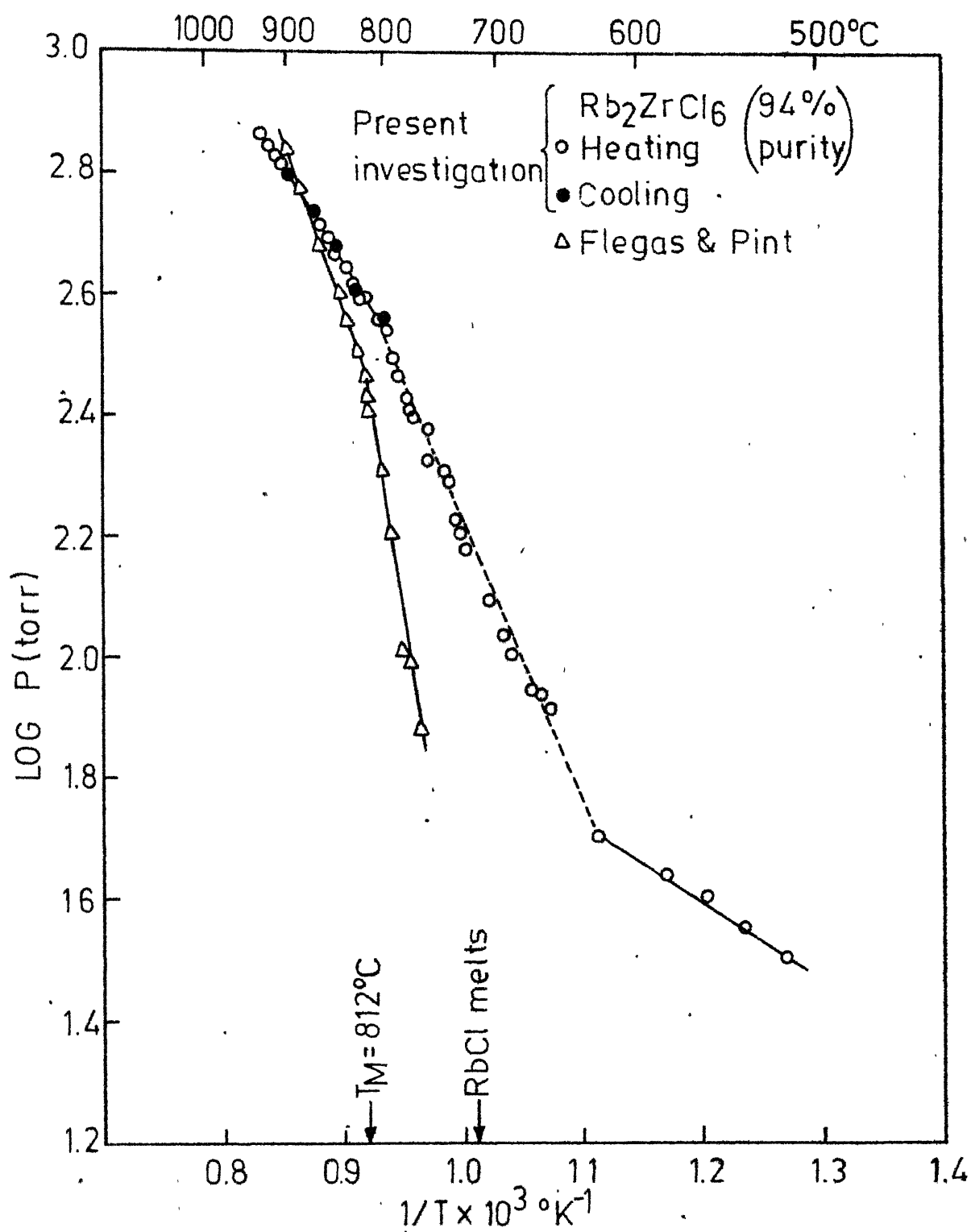


Fig.16 - Logarithmic vapour pressure of ZrCl_4 (torr) vs. $\frac{1}{T}$ ($^\circ\text{K}^{-1}$) over Rb_2ZrCl_6 .

well defined shape with abrupt changes of slope. The liquidus point indicated in the plot agrees well with the melting point reported earlier by Pint and Flengas.²⁰ The pressure values are also in good agreement at higher temperatures. The present data, however, indicate higher values at lower temperatures and a transformation at 633°C which may be the eutectic temperature.

Figure 17 shows the data for rubidium hexachloro hafnate (Rb_2HfCl_6). The abrupt changes of slope at 860°C may be due to the melting point. No data is available in the literature for this compound and no comparison can be made.

Figure 18 shows the vapour pressure data over the almost pure (98.18%) cesium hexachloro zirconate (Cs_2ZrCl_6). The melting points of the compound, cesium chloride and the eutectic, as reported in the literature are indicated by vertical arrows. The liquidus point of the compound as indicated in the plot agrees closely with that reported by Flengas and Pint.²⁰ The vapour pressure data also agree well with those reported by these authors. However, the present data indicate an opposite change of slope in the $\log P$ vs. $1/T$ plot at the liquidus. A slightly delayed eutectic formation is also indicated.

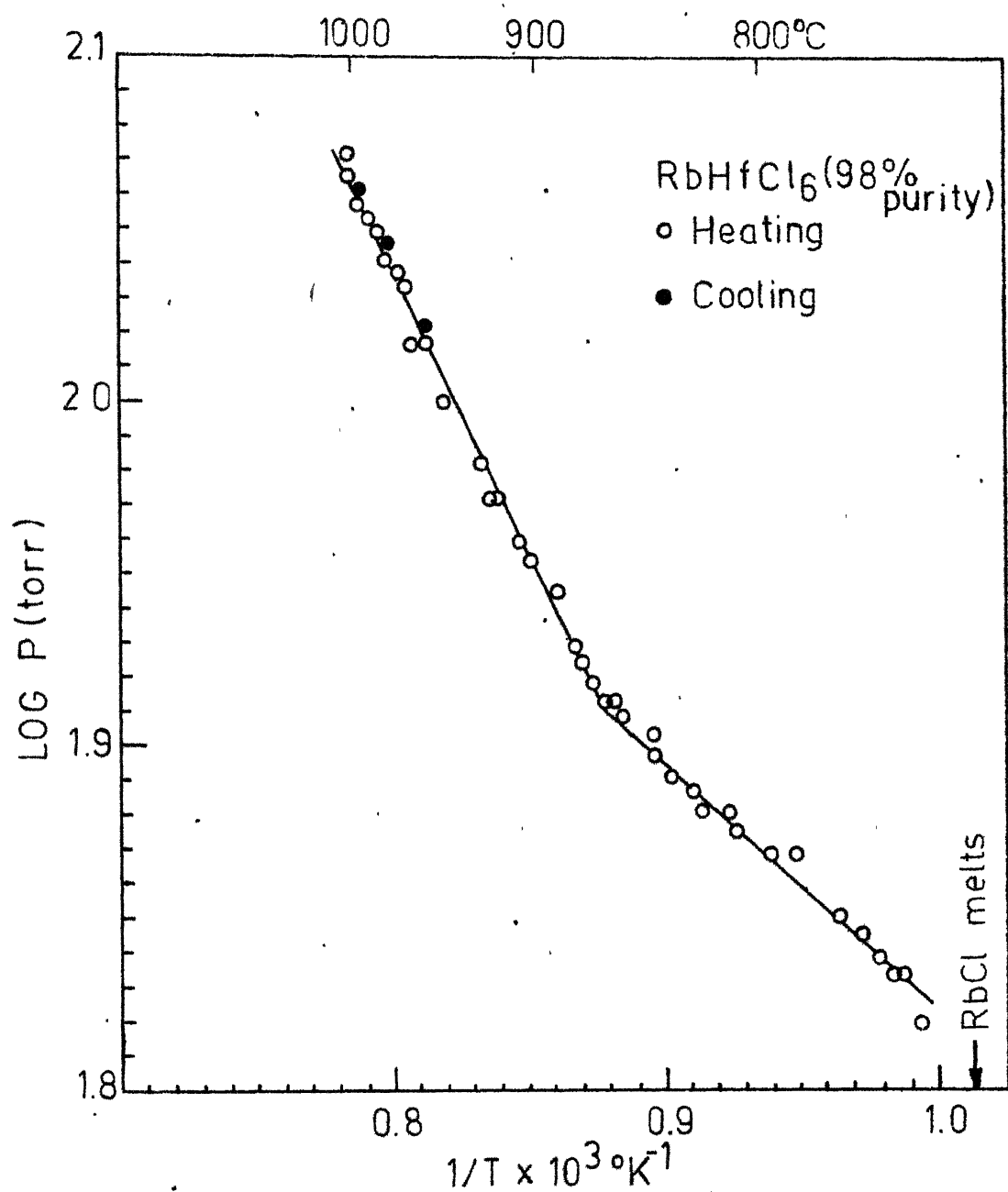


Fig.17 - Logarithmic vapour pressure of HfCl_4 (torr) vs $\frac{1}{T} (^\circ\text{K}^{-1})$ over Rb_2HfCl_6 .

Figure 19 shows the vapour pressure data over the almost pure (98%) cesium hexachloro hafnate (Cs_2HfCl_6). The figure also shows the data reported earlier by Asvestas¹⁸ and the melting temperatures for the hexachloro compound, cesium chloride and the eutectic. No abrupt changes of pressure, as reported by Asvestas have been observed in the present work. The melting point and the liquidus point indicated in the two plots are close although the vapour pressures differ significantly. The present data, moreover, indicate a delayed eutectic formation.

Table 3 summarises the vapour pressure data over the different systems in various ranges of temperatures. It also shows the equations reported in the literature.

It should be noted that the vapour pressure measurements were undertaken primarily to obtain values of pressures over the solid compounds at relatively low temperatures. Such data are not available in the literature. Since all the hexachloro compounds were somewhat impure (1.6 - 6% alkali chloride) it is understandable that the high temperature values do not give the correct pressures over the pure compounds. However, the uncertainty involved is small.

It may be interesting to compare the vapour pressures over either the zirconates or the hafnates as one goes from lithium to cesium. Flengas and Pirt²⁰ have tried to

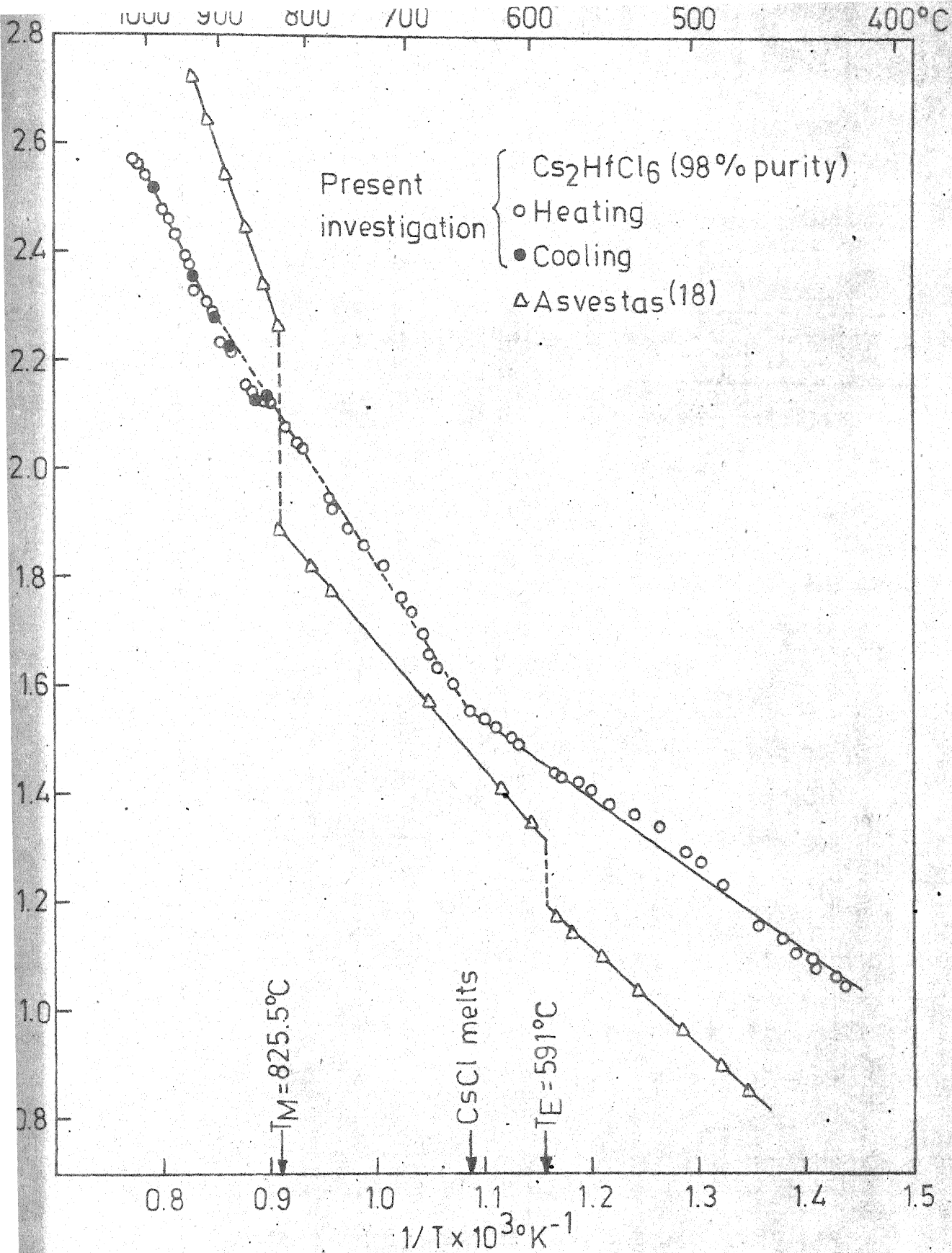


Fig. 19 - Logarithmic vapour pressure of HfCl_4 (torr) vs. $\frac{1}{T} (^\circ\text{K}^{-1})$ over Cs_2HfCl_6 .

Table III The equations of the lines, of the compounds investigated, have been obtained by a least square method. They are given below.

Compound	Equation of the line	Standard deviation	Temperature range (°C)
K_2ZrCl_6	$\log P = \frac{-3824.8}{T} + 5.9462$	0.087	481-713.5
	$\log P = \frac{-28762.4}{T} + 31.2639$	0.009	713.5-736.7
	$\log P = \frac{-1764.6}{T} + 4.5150$	0.026	736.7-819

K_2HfCl_6	$\log P = \frac{-2159.7}{T} + 4.426$	0.107	405-583
	$\log P = \frac{-3122.1}{T} + 5.6551$	0.072	583-792.2
	$\log P = \frac{-1815.3}{T} + 4.4232$	0.032	792.2-910

Rb_2ZrCl_6	$\log P = \frac{-1132.7}{T} + 2.9735$	0.063	518-633.5
	$\log P = \frac{-4645.0}{T} + 6.8631$	0.054	633-818
	$\log P = \frac{-0024.0}{T} + 2.7921$	2.187	818-932

Rb_2HfCl_6	$\log P = \frac{7576}{T} + 2.5788$	0.0379	735.4-860
	$\log P = \frac{0085.9}{T} + 2.0596$	4.7296	860-1004.2

Cs_2ZrCl_6	$\log P = \frac{-1295.2}{T} + 3.0962$	0.1164	419.3-621
	$\log P = \frac{-3071.3}{T} + 5.1004$	0.0754	621-869
	$\log P = \frac{-4434.9}{T} + 6.3183$	0.037	869-1028

Cs_2HfCl_6	$\log P = \frac{-1473.8}{T} + 3.1711$	0.1165	423-645
	$\log P = \frac{-2974.3}{T} + 4.7949$	0.079	645-913
	$\log P = \frac{-4101.9}{T} + 5.7605$	0.0226	913-1017

Literature data:

Compound	Equation of the line	temperature range (°C)	Reference
	$\log P = \frac{-18380}{T} + 19.83$	735-804	(20)
K_2ZrCl_6	$\log P = \frac{-4689}{T} + 7.12$	804-831	(20)
	$\log P = \frac{-11300}{T} + 13.4$	650-790	(19)
K_2HfCl_6	$\log P = \frac{-11830}{T} + 13.33$	700-790	(19)
	$\log P = \frac{-11900}{T} + 13.4$	760-812	(20)
Rb_2ZrCl_6	$\log P = \frac{-5350}{T} + 7.4$	812-903	(20)
	$\log P = \frac{-17200}{T} + 17.9$	777-817	(20)
Cs_2ZrCl_6	$\log P = \frac{-5030}{T} + 6.71$	817-1040	(20)
	$\log P = \frac{-11360}{T} + 11.80$	700-800	(19)
	$\log P = \frac{11930}{T} + 10.24$	740-820	(19)
Cs_2HfCl_6	$\log P = \frac{-2246}{T} + 3.925$	650-825.5	(18)
	$\log P = \frac{-5811}{T} + 7.555$	825-1000	(18)

correlate the temperatures at which pressure is one atmosphere (decomposition temperature) with ionic radii of alkali metal. Their data are plotted in Figure 20. The figure indicates a well defined relationship amongst the zirconate. The trend for hafnates is, however, anomolous. The same figure shows the data obtained in this investigation. These data, with the exception of the rubidium hexachloro hafnate, show excellent correlation. The data for zirconates match with that reported by Flengas and Pint.²⁰ The rubidium hexachloro hafnate shows abnormally low vapour pressure and has been eliminated from this figure. It may be concluded that the pressure data for rubidium hexachloro hafnate are not reliable.

Figure 21 shows the temperatures at which the pressure over the solid hexachloro compound reaches one-quarter atmosphere. This figure is plotted since, as discussed earlier, the pressures measured at lower temperatures are more reliable. This figure also shows a definite trend. It may be concluded at all temperatures and for alkalimetals the hexachloro hafnate is more stable than the hexachloro zirconates.

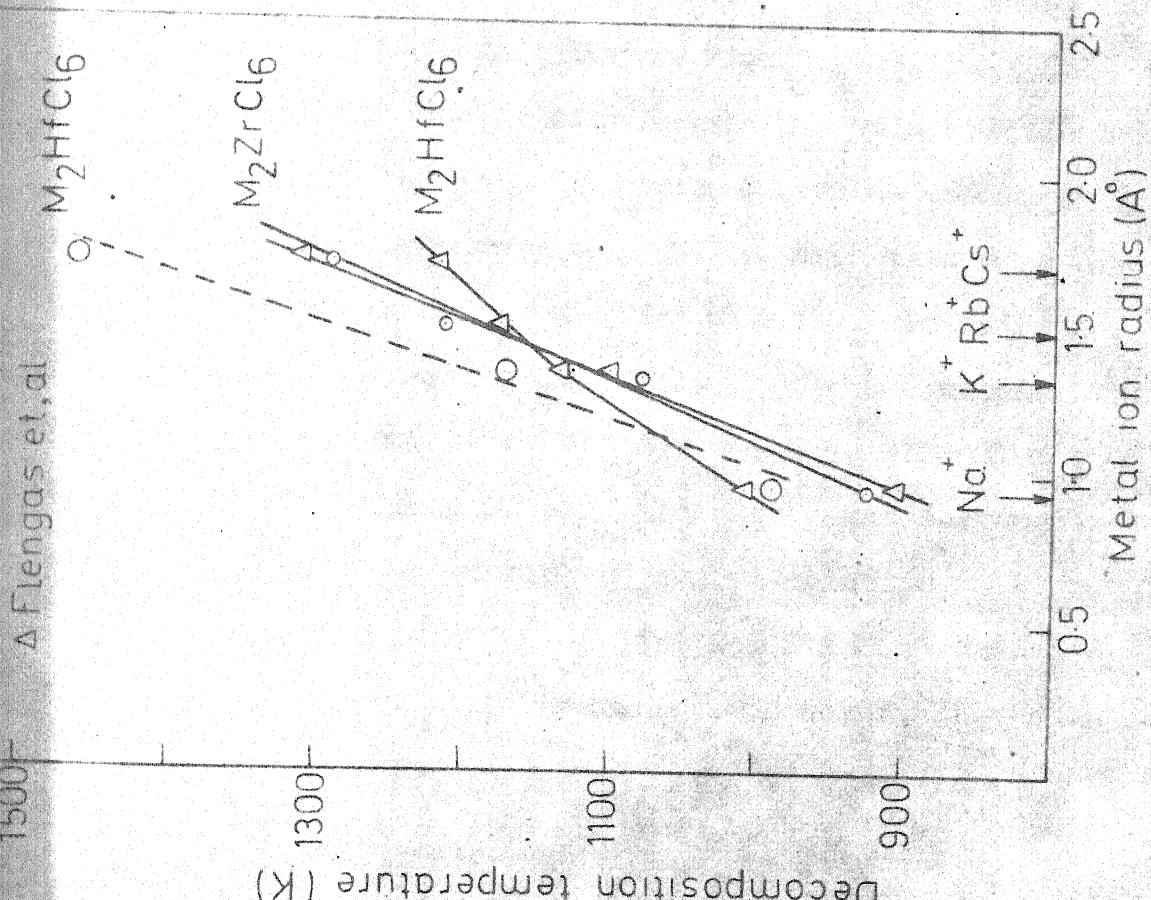


FIG.20 DECOMPOSITION TEMPERATURE OF COMPLEX COMPOUNDS VS METAL ION RADIUS

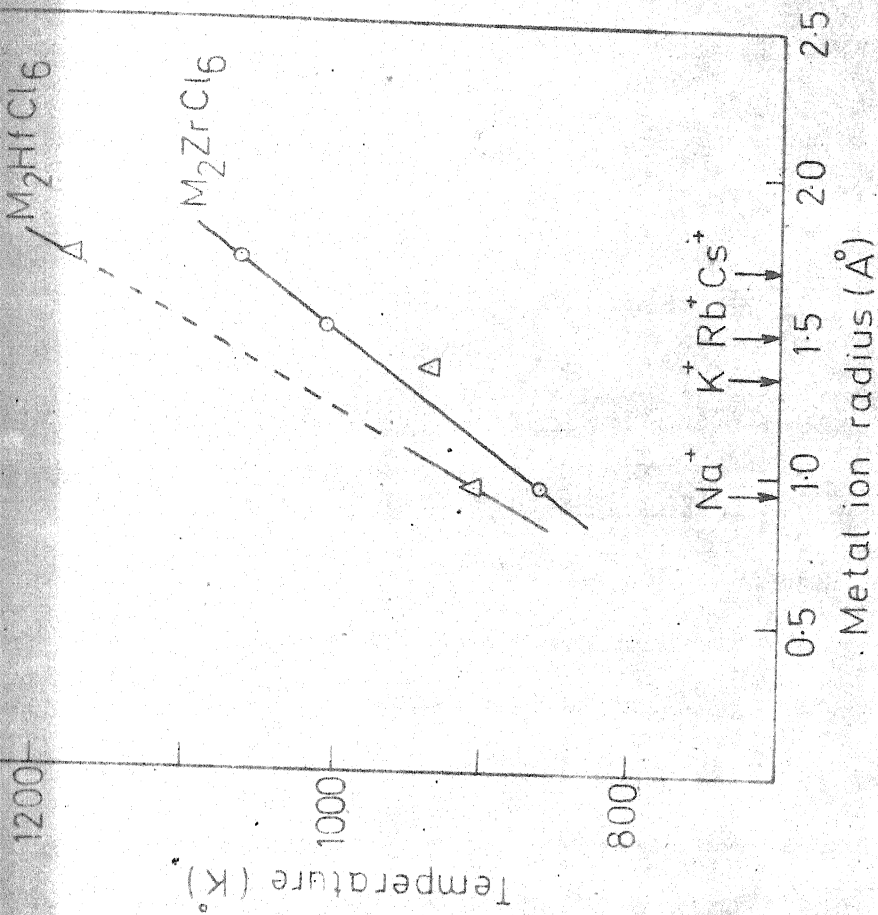


FIG.21 TEMPERATURE OF COMPLEX COMPOUND AT ONE-QUARTER ATMOSPHERIC VAPOUR PRESSURE VS METAL ION RADIUS

CHAPTER - 3

KINETIC STUDIES

3.1 Previous Kinetic Studies

Of the various alkali and alkaline earth metal chloro compounds of zirconium and hafnium, only the kinetics of formation of sodium compounds have been reported in the literature^{6,7}. Dutrizac and Flengas⁶ have studied heterogeneous kinetics of formation of Na_2ZrCl_6 using single crystal plates^{of} sodium chloride. The method consisted of measuring the weight gain for a single crystal of the salt when reacted with tetrachloride gas. A schematic diagram of the apparatus used is given in Figure 22. The weight gain measurements were done at stipulated intervals of time using a quartz spring from which the single crystal was hung by means of a fine platinum wire. Before the start of every run quartz spring was calibrated. The reaction was said to follow the well-known parabolic law. It was concluded that the reaction was controlled by diffusion of zirconium tetrachloride gas through the zirconate layer surrounding the inner core of the unreacted sodium chloride.

A subsequent study by Pint and Flengas⁷ on Na_2ZrCl_6 and Na_2HfCl_6 also reported. However, they assumed

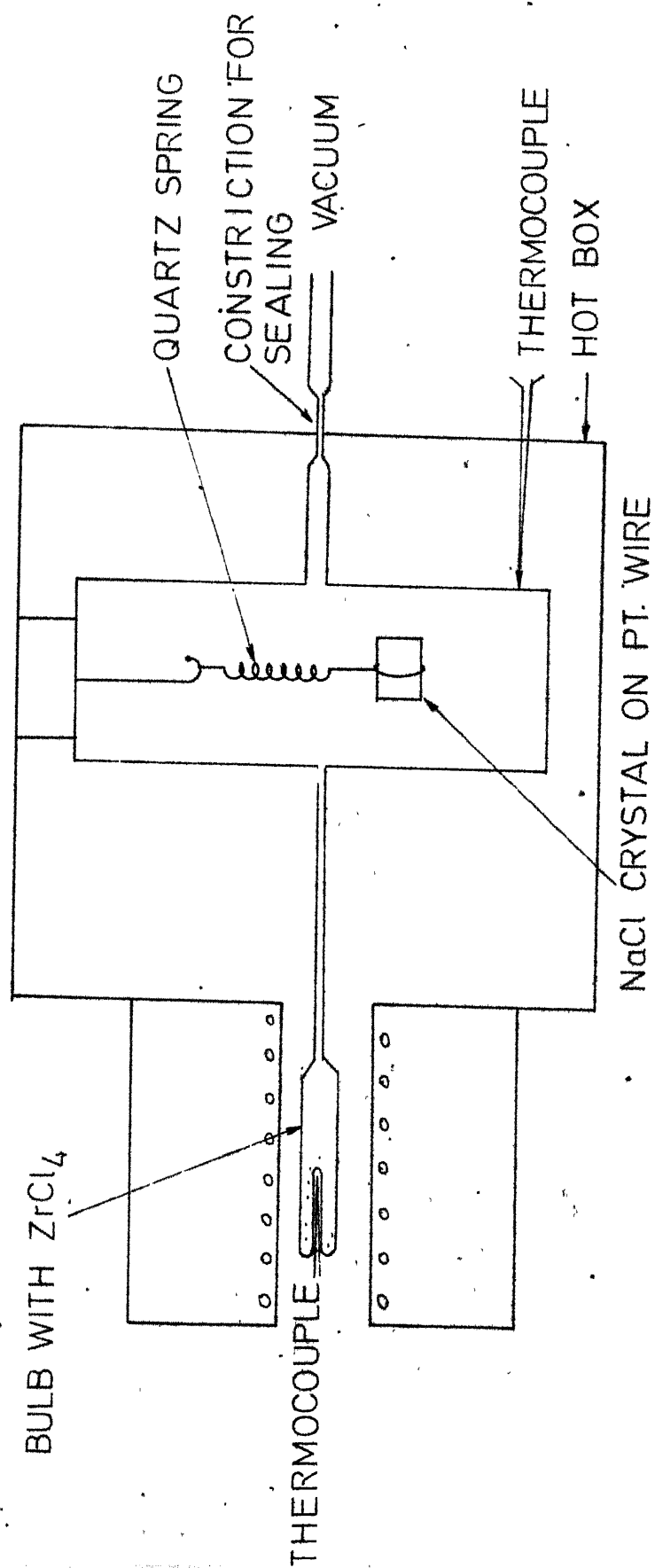


FIG. 22 APPARATUS FOR KINETIC INVESTIGATIONS (DUTRIZAC)

inward diffusion of chlorine ions instead of ZrCl_4 gas product phase transport control mechanism. The pressure dependence of the rate constant was studied for both cases at 485°C .

Subsequently Majumdar et al³⁻⁵ have done more systematic kinetic investigations in this laboratory. They have studied the kinetics of formation of the double compounds, Na_2ZrCl_6 and Na_2HfCl_6 using the principle of thermogravimetry in an all glass closed apparatus. A schematic diagram of the apparatus is given in Figure 23, which is self explanatory. Weight change was recorded by measuring the change in spring length. Their experiments were designed to study the effect of reaction temperature, gas pressure and sphere size on the rate of formation of the hexachloro compounds. Inert marker experiments were also carried out to aid the kinetic analysis. The kinetics of the formation reaction were found to be more favourable at higher gas pressure and higher reaction temperature and smaller sphere size. Majumdar et al have also studied the rate of reaction of HfCl_4 - ZrCl_4 vapour mixture with NaCl spheres and have shown that the reaction is controlled not by kinetic factors but by the exchange reaction



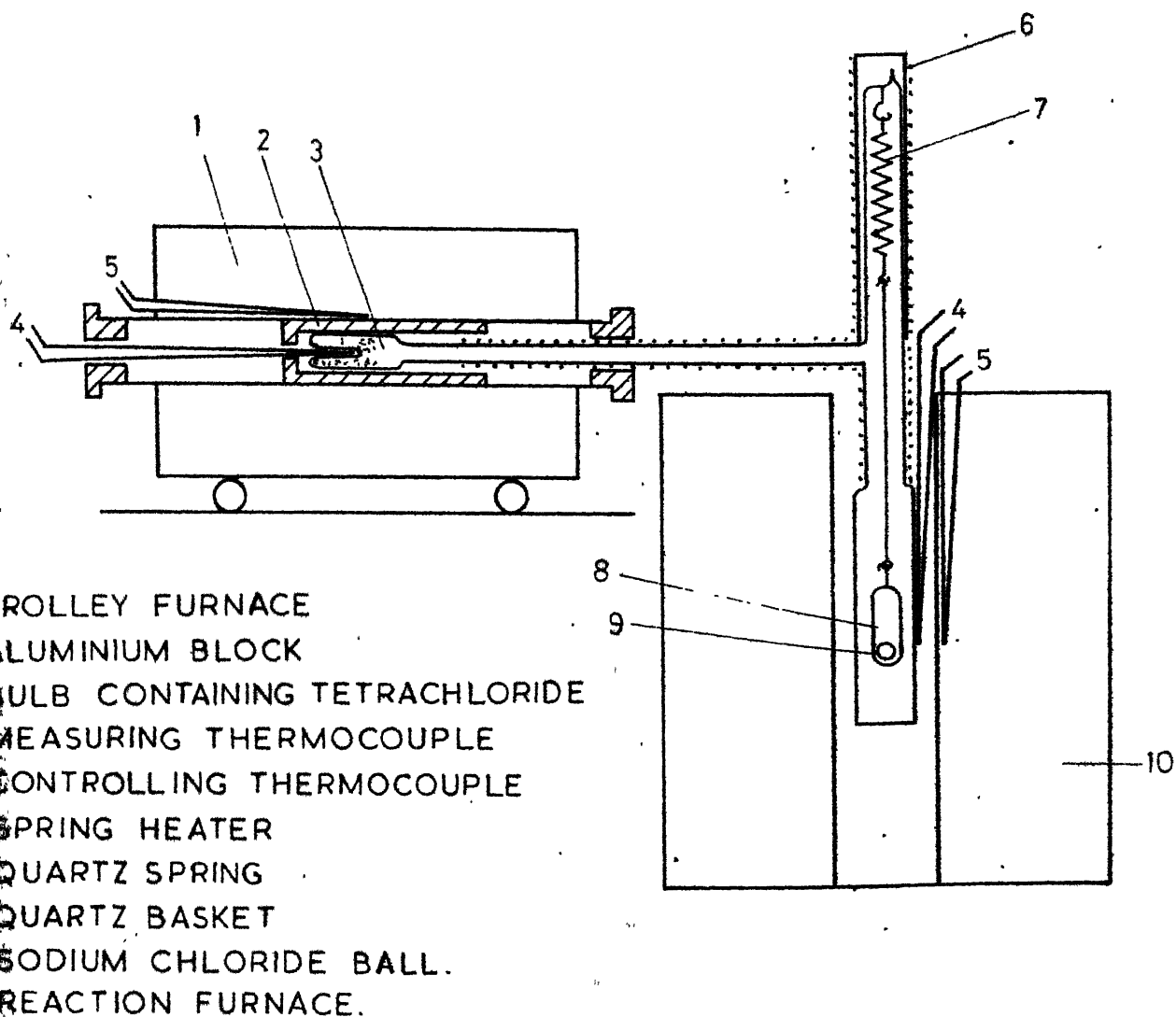


FIG.23 APPARATUS FOR KINETIC EXPERIMENTS

3.2 Reactions Involving Non-Porous Product Layer

If the reaction product is nonporous, the resistance by the boundary layer may be neglected as compared with the resistance through the solid product layer. If diffusion through the product is the rate limiting step and the reaction interface is plane, then the rate of chemical reaction i.e., the rate of the thickening of the product layer is inversely proportional to the thickness.

$$\frac{dy}{dt} = \frac{K'}{y} \quad (15)$$

where, K' is the reaction rate constant and y is the thickness of the product layer. Integration of equation (15) gives

$$y^2 = 2K't \quad (16)$$

This is the well-known parabolic law. If the solid is in the form of a sphere the above parabolic law will not hold because surface area for the reaction changes continuously during the reaction. A number of solutions²³⁻²⁹ of equation (16) have been proposed for spherical particles. There are three main rate equations for spherical particles; Jander's approximate equation, a simplified equation due to Crank, Ginstling and Brnnshtein and Carter-Valensi's exact equation.

(ii) Equation (17) is correct only if the volume unreacted core plus the volume of reaction product equals the volume of original material. This holds approximately true only at initial stages of the reaction.

b) Crank-Ginstling and Brounshtein simplified model^{24,25}

These workers developed a rate equation by taking a simplifying assumption that the volume change of the sample with time is zero. The equation is

$$\frac{2M_r DC}{\alpha_1 e_r r_o^2} = 1 - \frac{2}{3}F - (1 - F)^{2/3} \quad (19)$$

$$\text{or} \quad K_{GB} \cdot t = 1 - \frac{2}{3}F - (1 - F)^{2/3} \quad (20)$$

where, M_r is the molecular weight of the reactant, D is the diffusion coefficient, C is the concentration reagent and α_1 is the stoichiometry factor.

This equation has been found to give a better agreement than Jander's equation but still it fails at higher percentages of reaction because it does not take into account the change in the volume of the sample with time.

c) Carter-Valensi's exact solution²⁶⁻²⁹

The exact rate equation was developed independently by Carter and Valensi. The equation is

$$[1 + (Z - 1)F]^{2/3} + (Z - 1)(1 - F)^{2/3} = K_{cv}t \quad (21)$$

where, Z is the swelling parameter and K_{cv} is the reaction rate constant.

This equation has been found to hold upto 100 per cent of the reaction.

3.3 Aim of the Present Investigation

The present kinetic investigations have been carried out by allowing zirconium tetrachloride gas, at known partial pressure, to flow uniformly through packed beds of sodium chloride particles. The particle size of each bed has been in a well defined size range and the temperature of the bed has been accurately controlled. The rate of reaction has been obtained by measuring the weight gain at different intervals. Such packed beds are of greater industrial relevance than single pellets. The aim of the investigation is to examine if the well-known rate equations for the reaction of individual spheres are applicable to the present case of packed beds. An attempt is also made to examine the possibility of using the kinetic data reported by Majumdar³⁻⁵ for single spheres of sodium chloride in estimating the rates of reaction for packed beds under the conditions of the present work.

3.4 Experimental Technique

The apparatus used for kinetic investigations is shown in Figure 24. It has three main parts. In the first zirconium tetrachloride was sublimed in a furnace and introduced in a carrier gas (argon) under controlled conditions of temperature, flow rate of carrier gas, geometry of the bulb and enclosing tube etc. Previous work in the laboratory has shown that in the arrangement shown the partial pressure of ZrCl_4 in the gas stream does not change with time provided large amounts of ZrCl_4 are present in the bulb. It has also been shown that this arrangement yields the well-known plot of P_{ZrCl_4} versus flow rate plot with a well defined plateau region. The present work has been carried out at the flow rate of 200 cc per minute. For each run P_{ZrCl_4} has been determined from the actual loss in weight and prevalent flow rate of gas.

The second part of the apparatus consisted of a tube holding a batch of packed beds of different particle sizes. This arrangement exposes the different beds to the flowing gas under exactly identical conditions.

The last portion of the apparatus was provided for condensation of unreacted ZrCl_4 .

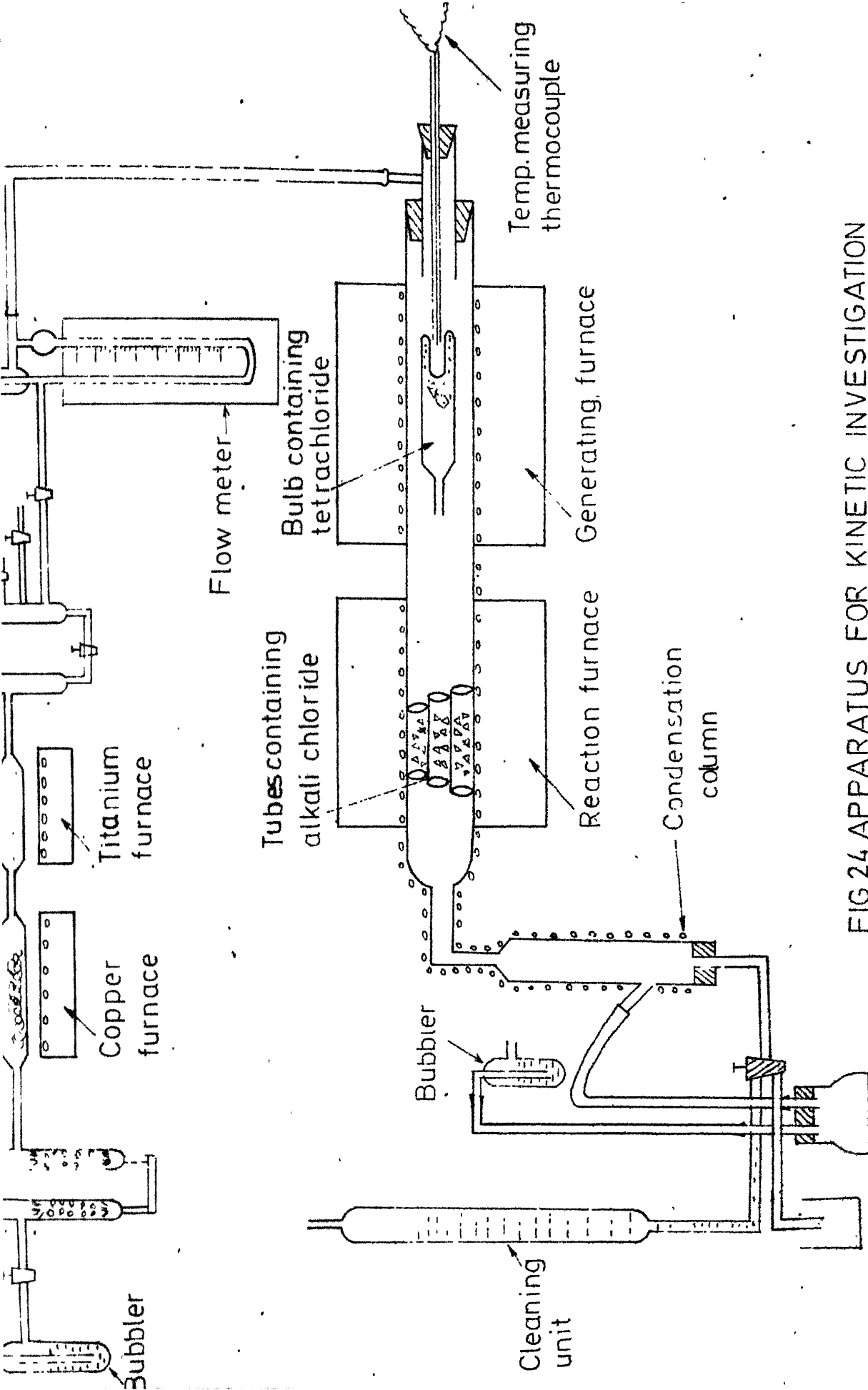


FIG 24 APPARATUS FOR KINETIC INVESTIGATION
BY TRANSPIRATION TECHNIQUE

3.4.1 Experimental procedure in the transpiration technique

To start with, the copper furnace was heated to 425°C , while the titanium furnace was heated to 700°C . And the generating furnace was heated to 280°C while the reaction furnace was heated to 450°C and maintained at the above mentioned temperatures for at least 2 hours before the start of experiment. After having well ensured that all the four furnaces were at required temperatures. The entire gas train was evacuated to 50 micron pressure and then the carrier gas was slowly admitted through the gas train to remove the water vapour present in the generating, reaction, and condensation chambers. This flushing was continued for about 10-15 minutes. The flow rate of the argon gas was maintained at 200 cc/minute. Next, the sodium chloride particles of three different sizes of known weight were loaded separately in three glass tubes of the same diameter 8.5 mm and three different lengths 14.5 cm, 15.5 cm, and 17 cms. Three different lengths were chosen to identify the solid NaCl particles corresponding to their lengths. The bed consisting of NaCl particles was covered by glass wool on either sides in the glass tube. Then these three glass tubes were loaded together into another glass tube of diameter 22 mm and length 16 cms. The length of the each bed was about 25 mm. The tube containing three beds

were introduced into the reaction furnace constant temperature zone. The solid ZrCl_4 was taken in a standard pyrex glass bulb (length 20 cms, well depth = 5 cms, dia. = 2 cms). The bulb was then introduced into the constant temperature zone of the generating furnace. Immediately the pre-heated and purified argon gas was admitted into the generating furnace. The four furnaces were maintained constantly at the above mentioned temperatures throughout the run. Solid ZrCl_4 sublimes at 280°C and gives out ZrCl_4 vapours which were carried away by the argon gas. The ZrCl_4 vapours pass through the three packed beds and react thereby to form sodium hexachloro zirconate. The reaction was continued for various lengths of time. To stop the experiment, the heat switch of the condensation column was put off and the excess of tetrachloride vapours condense in the condensation column. The ZrCl_4 glass bulb was taken out, stoppered. Then the tube containing three beds was taken out slowly and allowed to cooled in the desiccator. After cooling, the smaller tubes were taken out and weighed carefully to note the weight gain by sodiumchloride. After each run the three chambers were cooled down to room temperature and then washed thuro. out with water to collect the condensed tetrachloride. The result of the experiment are reported in Appendix II.

3.5 Results and Discussions

Preliminary results showed that the extent of solid-gas reaction under the conditions of present investigations is very small (0.6 to 8 per cent). For such limited extents of reaction the Jander's model²³ should be applicable for single spherical particles. Consider a bed of 'n' particles. If it is assumed that each particle is a sphere then each will react to the same extent for a given set of conditions. Jander's equation is

$$[1 - (1 - F)^{1/3}]^2 = K_j t$$

$$\text{i.e.,} \quad F = 1 - (1 - \sqrt[3]{K_j \cdot t})^3$$

when 'n' particles react we have

$$F_1 = F_2 = \dots = F_n$$

$$\therefore nF = n[1 - (1 - \sqrt[3]{K_j t})^3]$$

$$\text{i.e.,} \quad F = 1 - (1 - \sqrt[3]{K_j t})^3$$

This equation indicates that the same Jander's equation is valid for a packed bed also provided

(a) each polygonal particle be assumed to be a sphere, and

- (b) the extent of reaction be so small that each particle retains its identity and surface area.

3.5.1 Establishment of a fixed P_{ZrCl_4} in flowing gas stream

Figure 25 shows the weight loss from a ZrCl_4 filled bulbs versus for different periods of time. Each point correspond to an entirely independent run. It should be noted that the ZrCl_4 filled bulb cannot be re-inserted once it has been taken out for weighing to measure the weight loss. It has been observed that the ZrCl_4 surface tends to become inactive while in the process of being taken out without measurable change in weight. The figure clearly shows that the rate of weight loss is almost reproducible from run to run and remains uniform over periods at, at least as large as 40 hours provided the geometry of the system, the flow rate of carrier gas and the temperature of the bulb are kept constant as is the case in the present investigation. It is, therefore, concluded that the partial pressure of ZrCl_4 is uniquely defined by the experimental conditions. Because

$$P_{\text{ZrCl}_4} = \left(\frac{n_{\text{ZrCl}_4}}{n_{\text{ZrCl}_4} + n_{\text{Ar}}} \right) \times \text{Total pressure.}$$

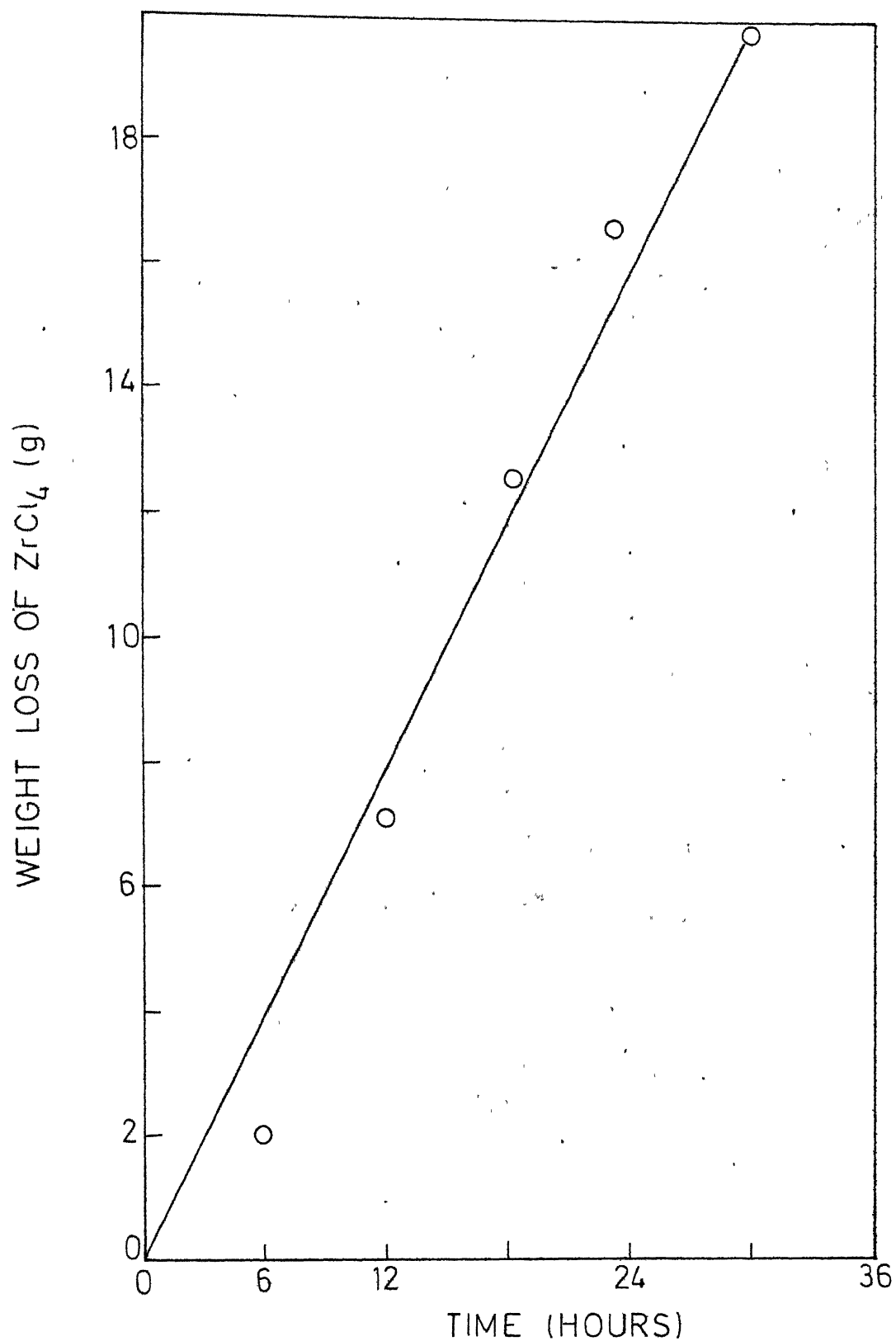


FIG 25 WEIGHT LOSS OF ZrCl_4 VERSUS DIFFERENT PERIODS OF REACTION TIME.

In the present investigation the value of average P_{ZrCl_4} has been calculated for each run from the actual weight loss observed.

Figure 26 illustrates the kinetic data, according to the Jander's model, for four different average sizes of particles. The particle sizes shown represent the average particle size based on root mean square size, in the range (- 6 + 8) mesh to (- 14 + 45) mesh etc. The large deviations from linearity in the case of the smallest sized particle may be attributed to the uncertainty in one of the three data (first point) as well as the fact that the model is more applicable for larger particle sizes. The figure also shows that the fraction reacted for a given interval increases as the particle size decreases. In all cases a small incubation period is indicated and, therefore, the lines do not pass through the origin. This initial period of incubation may be attributed to the uncertain time needed to establish uniform temperatures after insertion of the $ZrCl_4$ bulb into the furnace. This may also be due to a time lag for the beginning of the reaction itself. It may be noted that small incubation periods in gas-solid reactions has often been reported in the literature. It is also interesting to note the incubation period seems to decrease as we go from the large size to the small sizes. Figure 27 shows the

trend. Data from the smallest size has been disregarded for this plot because of the previously mentioned anomaly.

Table IV Incubation periods, slope of the lines for various sizes of NaCl particles according to Jander's equation (Figure 26)

Size of the NaCl particle (d_o) mm	Incubation period hours-minutes	Slope of the line 10^6 (hr^{-1})
2.886	4-06	1.16
2.048	2-54	1.46
1.448	1-36	4.00
0.864	ZERO	25.00

The slope is constant K_j which depends on the nature of the solid, the reaction and the size of the particle. A master constant can be calculated by incorporating into the equation the particle size. Since the rate of the reaction is proportional to the surface area of particles available, the master constant should be $K_j \cdot d_o^2$. That is the master constant K ,

$$K = K_j \cdot d_o^2 = \frac{i}{t} d_o^2$$

Table V, lists the master constants as calculated from each individual data. They are all of the same order.

1 PARTICLE (NaCl) SIZE (d₀) = 2.886 mm

1 " " (d₀) = 2.348 mm
 1 " " (d₀) = 1.448 mm
 2 " " (d₀) = 0.864 mm

120
80
40
0

$[1-(1-F)^{1/3}]^2 \times 10^6$

$[1-(1-F)^{1/3}]^2 \times 10^6$

200
400
600
800

Time, hours

FIG 26 PLOTS OF EXPERIMENTAL DATA ACCORDING TO JANDER'S EQUATION FOR VARIOUS SIZES OF SODIUM CHLORIDE PARTICLES

INCUBATION PERIOD, HOURS

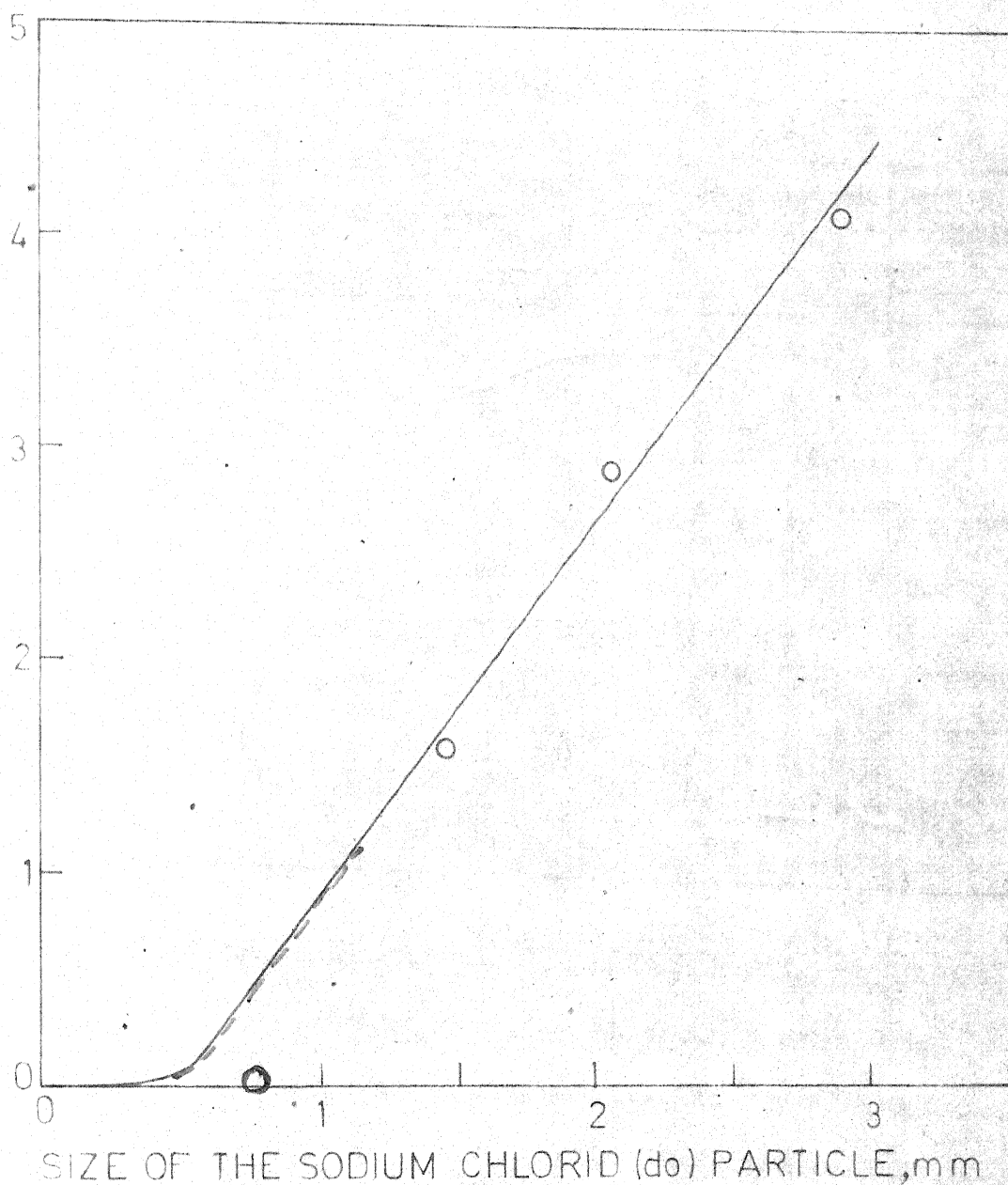


FIG 27 INCUBATION PERIODS Vs SIZE OF THE SODIUM CHLORIDE PARTICLES ACCORDING TO JANDER'S EQUATION

Table V Master constant (K)

Size of NaCl particle \bar{d}_o (mm)	Run	Master constant, K $\times 10^6$ (mm^2/hr)	Rate constant $K_{cv} \times 10^4, \text{hr}^{-1}$	$K' \times 10^4$
2.886	13	2.96	0.00337	0.6587
	19	7.50	0.01154	2.0764
	8	8.437	0.01336	2.3506
	16	8.05	0.01233	2.2713
2.0484	1	2.99	0.01149	1.1473
	2	4.257	0.01185	1.5190
	5	5.564	0.0177	2.2739
1.448	14	7.667	0.0467	2.2939
	20	7.85	0.0475	2.1520
	17	8.179	0.0493	2.2848
0.864	15	18.90	0.0315	0.5499
	21	20.99	0.0344	0.5541
	18	18.60	0.0397	0.6541

3.5.2 Comparison with the single sphere studies

Earlier studies by Majumdar et.al.,³⁻⁵ involving reaction of single spheres of sodiumchloride with zirconium tetrachloride gas had to be interpreted in terms of the Carter-Valensi equation (eqn. 21), because of high percentage of reaction (as large as 90%) and large swelling which resulted from it. Their results indicated that the dependence of K_{cv} on the experimental conditions may be written as the following.

$$K_{cv} \propto P^{1/2} \quad (22)$$

$$\ln K_{cv} \propto -1/T \quad (23)$$

and

$$K_{cv} \propto \frac{1}{d_o^2} \quad (24)$$

Combining these equations we may write

$$K_{cv} = \frac{K' \cdot P^{1/2} \cdot \exp(-7.5 \times 10^3/RT)}{r_o^2} \quad (25)$$

An analysis of his data is summarised in Table VI which gives the value of K' as defined by equation 25. It should

Table VI Carter-Valensi rate constants for the formation of Na_2ZrCl_6

Effect of	Sphere size r_o , mm	temperature (°C)	Pressure P_{ZrCl_4} (torr)	Rate constant $K_{cv} \times 10^4$, hr ⁻¹	$K' \times 10^3$ calculated in the present investigation
Pressure	6.041	450.0	257	1.757	72.45
	6.089	451.0	381.0	2.158	74.3
	6.089	451.0	520	2.630	77.5
	6.078	450.5	745	2.968	72.8
	6.087	450.5	1013	3.560	75.1
Temperature	6.078	425.0	745	2.375	71.2
	6.078	450.5	745	2.968	72.8
	6.075	475.3	753	3.456	68.9
	6.089	500.0	734	4.031	74.1
Sphere size	3.303	450.0	739	9.575	69.7
	4.614	451.0	753	5.027	70.7
	6.078	450.5	745	2.968	72.8

be noted that this is not identical to the master constant (K) obtained in the present investigation because of the difference in models used. However, one can obtain K' for the present data by applying the Carter-Valensi equation.

The Table V shows the values of K_{cv} as obtained by applying Carter-Valensi equation to the present data. The values of K' as obtained from this K_{cv} by substituting for the actual values of pressure, particle size and temperature are also given in the table. It is seen that K_{cv} values for the present investigation is very small. It also shows that K' values as obtained in the present investigation are more than two orders of somewhat magnitude smaller. The discrepancy would be less if one takes into account the incubation period. However, it will still remain the same order. This discrepancy presumably is not due to the very small particle size. It must be attributed to a different mechanism prevalent at low pressures and initial stages of the reaction. For example the pressure dependance may be different and the activation energy for the reaction may also differ significantly from the value given by Majumdar.

It may be concluded that the rates of reaction in initial stages are low compared to the rates reported earlier for single pellet experiments involving high pressures of $ZrCl_4$ and larger percentages of reaction. Although the experimental data fit the diffusion model proposed by Jander no firm conclusion can be drawn regarding the reaction mechanism because of the inadequacy of data.

CHAPTER - 4

REACTOR DESIGN AND FABRICATION

4.1 Introduction

A reactor for the separation of hafnium from zirconium by fractional sublimation of the hexachloro compounds was designed and fabricated. The reaction in the reactor is of heterogeneous in nature (i.e., solid-gas) and extremely slow. Hence a continuous exposure of fresh solid surface to the gas phase would help increase the reaction rate. Further, as the reaction is known to be diffusion controlled³⁻⁵, the stripping of product phase from the solid would facilitate the contact of reactive vapours with the unreacted core of the solid. Both purposes e.g., continuous exposure of new surface of the solids and continuous removal of the product phase from the unreacted core could be achieved by using a screw conveyor reactor. In a screw conveyor, screw shaft rotates continuously forcing the solid particles to roll and collide all time. The path is around the axis of the screw shaft. The screw shaft was designed for forward movement, continuous drive and reversal of the movement by changing the direction of rotation of the screw shaft by incorporating a suitable

switch and changing the inclination of pipe to the desired angle.

4.2 The Reactor Assembly

The reactor assembly is shown in Figure 28. The different parts are shown in Figure 29. The reactor was designed to have three feed inlets either for solids or gas. Two such inlets are near the end while the third is in the middle of the reactor. All are in line along the axis. Four gas sample collectors are in one line are also provided. Each is situated at about 30 cm from the next and inclined at an angle of 45° to the feed inlets.

There is a screw shaft which rotates in the reactor body in order to carry out the solids from one end to the other. The direction of material flow can be reversed by reversing the inclination of the reactor and by changing the direction of rotation of the screw. The reactor is firmly held in position by three sets of mild steel specially fabricated clamps (Figure 29, j). This minimizes the vibration of the reactor. The screw shaft rotates on two ball bearings. The gear box shown in the figure gives a reduced speed (17 r.p.m.) of rotation of the shaft. The inclination of the reactor can be changed as desired.

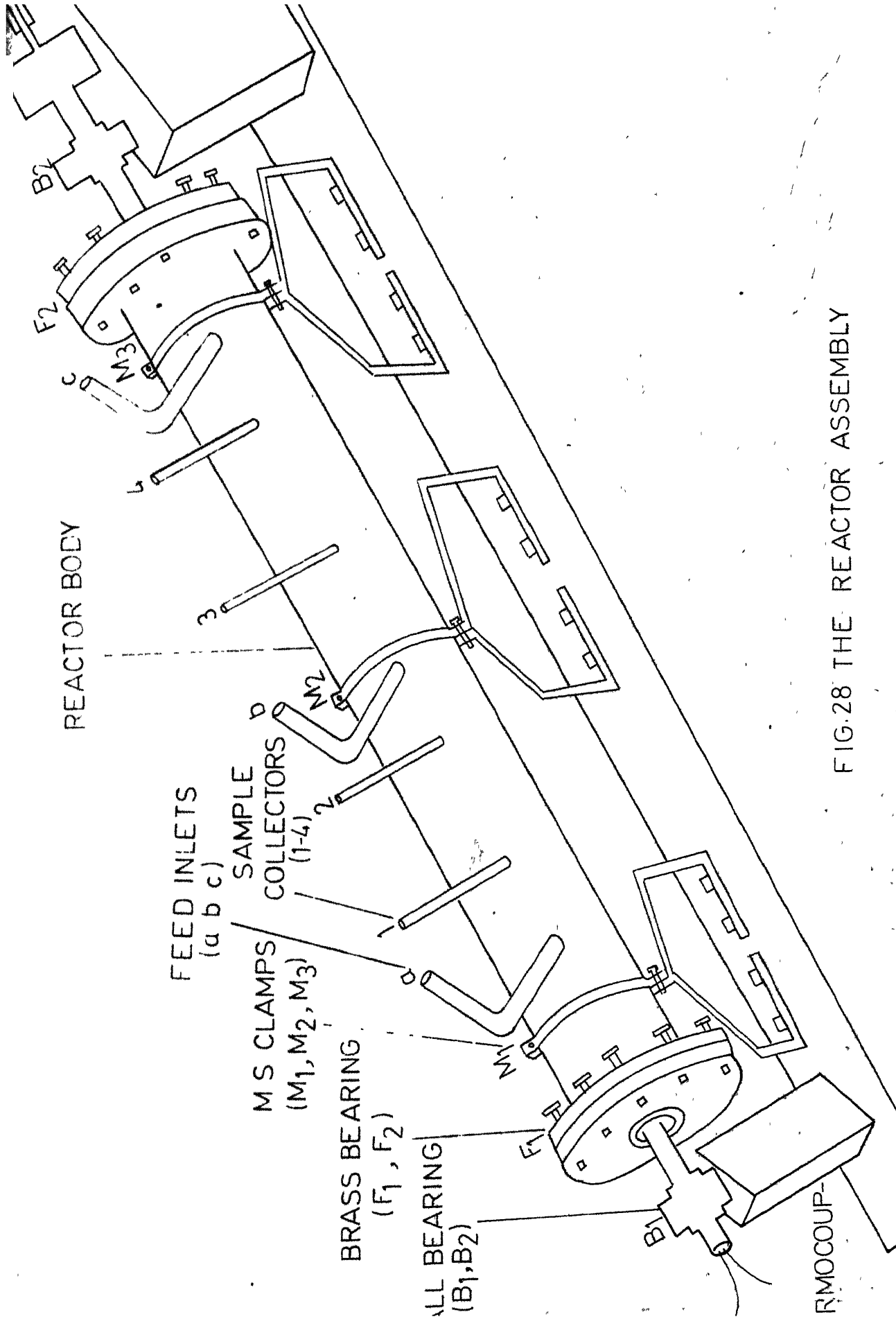
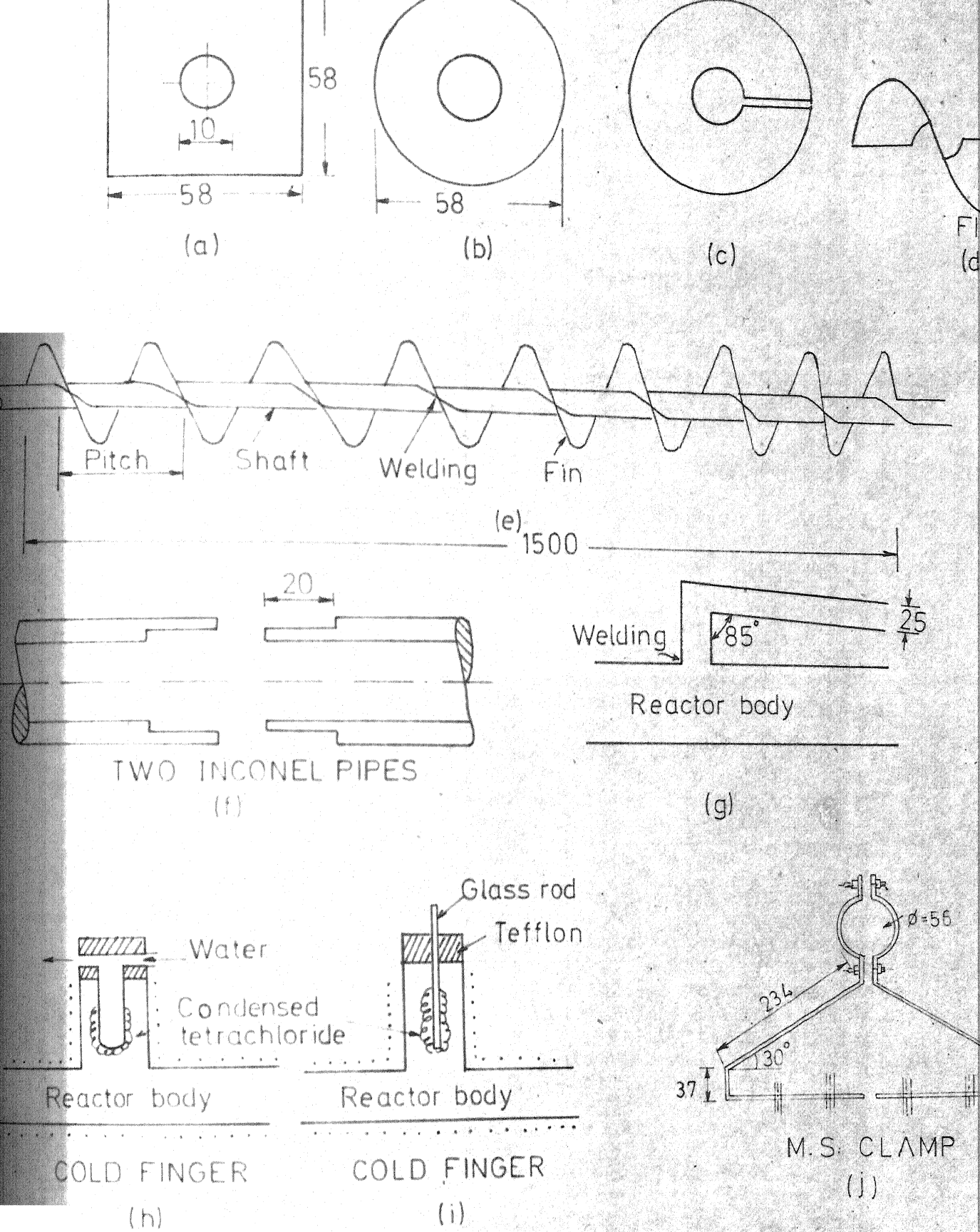


FIG. 28 THE REACTOR ASSEMBLY



All dimensions are in mm

FIG 29 THE VARIOUS PARTS OF REACTOR

4.3 The Details of Various Parts

- (a) The screw shaft: This is shown in figure 29(e). The screw was made from specially shaped pieces cut from a stainless steel sheet 3.2 mm thick. Square pieces of size $5.8 \times 5.8 \text{ cm}^2$ were cut. Then holes of diameter 10 mm were drilled at the centre of such squares (Figure 29(a)). Squares were mounted on a mandrel of the lathe machine and machined to make circular discs of diameter 5.05 cm (Figure 29,b). The discs were cut along the radius as shown in Figure 29,c. Subsequently the disc was twisted to form a helical fin as shown in Figure 29,d. Such fins were mounted on a hollow stainless steel tube of external diameter 10 cm and length 205 cm. Two fins were brought close to each other and joined by welding. The fins were also welded to the hollow stainless steel tube. This welding was continued for a length of about 1.5 meter. The screw shaft was bent very much due to the thermal stresses induced while welding the fins over the hollow stainless steel tube. It was straightened out after fixing in a wooden frame and then polished.
- (b) The reactor body: The main body of the reactor was made by joining two inconel pipes of diameter 6.4 cm

and 90 cm length as shown in Figure 29,f. The three feed inlets (shown in Figure 29,g) made of stainless steel tubes of diameter 25 mm and length 24 cm, were joined at nearly right angle (85°) to each other by welding. Four stainless steel tubes of external diameter 8 mm, length 15 cm were also joined by welding to the main body about 30 cm each apart in a line parallel to the axis of the body and inclined at an angle of 45° to the vertical feed inlets. These four tubes were meant for the collection of ZrCl_4 - HfCl_4 samples. The sample collectors have been designed to incorporate 'cold fingers' as shown in Figure 29,h and i. The cold finger of kind shown in Figure 28,h, can be used in any two of the three feed inlets. Cold finger of the kind shown in Figure 29,i, can be used in the four sample collectors. Brass flanges incorporating 'O'-ring were fabricated and joined to the main body on either ends by brazing. The outer flange consists of the groove for the 'O'-ring and a Teflon circular bead to prevent the escape of gases during operation.

CHAPTER - 5

CONCLUSIONS

The main conclusions of the work are the following.

1. It is possible to prepare the hexachloro compounds of the type M_2ZrCl_6 and M_2HfCl_6 , where M is an alkali metal, by reacting finely powdered alkalichloride (about -100 mesh) with vapours of $ZrCl_4$ or $HfCl_4$ at temperatures of around $450^\circ C$ and pressures of about 1 atmosphere. The reactions are however not complete even after repeated grinding and the reaction. After four or five cycles, reactions upto about 99% may be achieved.

2. The tin isoteniscope method is ^a suitable method for measuring vapour pressures over the volatile compounds with an accuracy of ± 1 torr. However ^{uncertainty} This accuracy is below the uncertainty due to uncertainty of the solid temperature is comparable to that due to the temperature fluctuations in the solid.

3. The vapour pressure of $ZrCl_4$ or $HfCl_4$ over the corresponding ^{solid} hexachloro compounds is unaffected by the presence of alkalichloride impurity, because the pressure over the latter is negligible in the temperature ranges employed. The low temperature data of the present investigation, therefore, ^{may be} considered reliable.

Since the mixture of the compound and the alkali-chloride impurity (1 to 5%) is not an equilibrium system above the eutectic temperatures, the data for higher temperatures are questionable. In several runs, however, an eutectic transformation is indicated at temperatures close to that reported in the literature for melting of the eutectic. In some other runs a delayed transformation is indicated presumably because of kinetic factors.

4. The vapour pressure data over the solids at low temperatures are not available in the literature and, therefore, the reliability of the present data cannot be assessed by comparison.

5. The present data show that the hexachloro hafnates of all the alkali metals studied (K, Rb, Cs) are more stable than the corresponding hexachloro zirconates. Moreover the stability increases in a definite manner with cation size. The temperatures at which the vapour pressure of the tetrachloride reaches a fixed values (1 atm, or $\frac{1}{4}$ atm) vary almost linearly with ^{the} cationic radii. The present data are consistent with values reported by Bhat² in this respect. The data measured for Rb_2HfCl_6 , however, do not fit into the trend and must be rejected as unreliable. The uncertainty in this case may be ascribed to incomplete removal of trapped gases prior to the vapour pressure measurements.

6. The vapour pressure data, and the greater stability of the chloro hafnates indicate ^{that} it is possible to separate zirconium from hafnium for fractional sublimation, provided the technical problems are surmounted. The latter implies mainly problems associated with handling of the reactive compounds (both solids and gases), sampling ^{of} gases, rates of reaction etc. Since the reaction rate is slow in all cases, the method would be primarily ^{an} thin film sublimation'.

7. The present measurements also confirm the very high stabilities of cesium and rubidium compounds. These compounds, therefore, would be suitable for molten salt electrolysis for electrolytic production of Zr and Hf. The stability would be further enhanced if the hexachloro-compounds ~~is~~ dissolved in sodium chloride and/or in potassium-chloride.

8. The kinetic studies show that, although the reaction rate is very small it is possible to use the transpiration technique for investigating the kinetics of the initial stages of the reaction. The initial kinetics which may differ from that in the subsequent stages are relevant from the point of view of thin film sublimation.

The kinetic data show that the initial stages of reaction may be understood in terms of the Jander's model for gas-solid reactions. In this model the reaction is assumed to be taken place through a diffusional process.

9. In all kinetic runs for weight gain measurements, there is an incubation period. This period, which is found to decrease with the particle size may be attributed to the time required for attainment of a steady temperatures after insertion of the cold solids in the furnace.

10. The master constant calculated as $\frac{x_d^2}{t_0}$ varies, for all runs, within a reasonable range (3×10^6 to 21×10^6) which further substantiate the validity of the Jander's model.

11. The earlier kinetic data obtained for reactions of single spheres with tetrachloride gases were analysed in terms of the Carter-Valensi equation. The present data, however, have not been so analysed because of the small extents of reaction. However, K_{CV} values have been calculated for all runs. From these values it is possible to calculate the constant K' , which is independent of the particle size, temperature and pressure. These values are, however, not consistent with similar values calculated from earlier data on single spheres and large extents of reaction.

It may be concluded that the mechanism of reaction in the earlier stages is different from that prevalent in later stages. It is not possible to discuss this in detail due to the inadequacy of data.

The kinetic data show very small extents of reaction under the experimental conditions used (pressure approximately = 3 to 6 torr, temperature = 450°C, particle sizes 0.864 mm to 2.886 mm). This means that the fractional sublimator will have to make provisions for increased reaction rates.

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APPENDIX - IVAPOUR PRESSURE DATA OF ZIRCONIUM TETRACHLORIDE OVER THE
POTASSIUM HEXACHLORO ZIRCONATE (K_2ZrCl_6)

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
1	481.0	754.0	1.3263	7.5	0.8751
2	494.0	767.0	1.3038	9.2	0.9638
3	499.8	772.8	1.2939	9.5	0.9777
4	506.5	779.5	1.2829	10.5	1.0212
5	513.9	786.9	1.2708	11.5	1.0607
6	521.0	794.0	1.2594	12.5	1.0969
7	526.5	799.5	1.2508	13.1	1.1173
8	530.0	803.0	1.2453	15.5	1.1903
9	537.0	810.0	1.2346	17.0	1.2304
10	541.5	814.5	1.2278	18.0	1.2553
11	548.9	821.9	1.2167	19.0	1.2788
12	553.0	826.0	1.2107	22.0	1.3424
13	559.0	832.0	1.2019	22.5	1.3522
14	562.0	835.0	1.1976	25.0	1.3979
15	565	838.0	1.1933	26.0	1.4150
16	567.0	840.0	1.1905	27.0	1.4314
17	573.0	846.0	1.1820	30.0	1.4771
18	581.0	854.0	1.1709	32.0	1.5051
19	588.5	861.5	1.1608	34.0	1.5315
20	596.0	869.0	1.1507	37.0	1.5682
21	602.5	875.5	1.1422	39	1.5911
22	611.0	884.0	1.1312	42.0	1.6232
23	619.9	892.9	1.1199	46.0	1.6628
24	627.0	900.0	1.1111	49.0	1.6902
25	633.5	906.5	1.1031	52.0	1.7160
26	647.0	920.0	1.0869	56.0	1.7482
27	659.0	932.0	1.0729	67.0	1.8261
28	674.0	947.0	1.0560	78.0	1.8921
29	680.5	953.5	1.0488	86.0	1.9345
30	687.0	960.0	1.0417	90.0	1.9542
31	694.0	967.0	1.0341	96.0	1.9823
32	701.5	974.5	1.0262	100.0	2.0000
33	713.5	986.5	1.0137	110.0	2.0414
34	708.6	981.6	1.0188	140.0	2.1461

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
35	720.0	993.0	1.0070	180.0	2.2553
36	724.5	997.5	1.0025	285.0	2.4548
37	726.0	999.0	1.0010	310.0	2.4914
38	729.4	1002.4	0.9976	400.0	2.6021
39	734.0	1007.0	0.9930	480.0	2.6812
40	734.6	1007.6	0.9925	540.0	2.7324
41	736.7	1009.7	0.9904	565.0	2.7520
42	739.0	1012.0	0.9881	590.0	2.7709
43	744.0	1017.0	0.9832	600.0	2.7853
44	752.0	1025.0	0.9756	640.0	2.8062
45	768.0	1041.0	0.9606	655.0	2.8162
46	773.0	1046.0	0.9560	680.0	2.8325
47	781.3	1054.3	0.9485	700.0	2.8451
48	790.6	1063.6	0.9402	710.0	2.8513
49	801.0	1074.0	0.9311	750.0	2.8751
50	807.0	1080.0	0.9259	759.9	2.8807
51	819.3	1092.3	0.9155	780.0	2.8949
While cooling					
52	810.7	1083.7	0.9228	770.0	2.8865
53	787.0	1060.0	0.9434	748.0	2.8739
54	731.8	1004.8	0.9952	516.0	2.7127

VAPOUR PRESSURE DATA OF HAFNIUM TETRACHLORIDE OVER THE
POTASSIUM HEXACHLORO HAFNATE (K_2HfCl_6)

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
1	405.0	678.0	1.4749	15.0	1.1761
2	414.0	687.0	1.4556	17.0	1.2304
3	419.3	692.3	1.4445	18.5	1.2672
4	424.8	697.8	1.4331	20.0	1.3010
5	431.6	704.6	1.4192	22.0	1.3424
6	443.2	716.2	1.3965	24.5	1.3892
7	459.0	732.0	1.3661	30.0	1.4843
8	465.3	738.3	1.3545	33.5	1.5250
9	471.3	744.3	1.3435	36.0	1.5563
10	478.0	751.0	1.3316	38.0	1.5798
11	487.8	760.8	1.3144	40.0	1.6021
12	496.0	769.0	1.3004	44.0	1.6435
13	510.8	783.8	1.2758	53.0	1.7243
14	521.6	794.6	1.2585	62.0	1.7924
15	543.0	816.0	1.2253	78.0	1.8921
16	551.0	824.0	1.2136	80.0	1.9031
17	567.4	840.4	1.1899	86.0	1.9345
18	573.0	846.0	1.1820	89.0	1.9518
19	583.0	856.0	1.1682	97.0	1.9868
20	591.8	864.8	1.1563	105.0	2.0212
21	598.3	871.3	1.1477	120.0	2.0792
22	607.2	880.2	1.1361	125.0	2.0969
23	619.0	892.0	1.1211	142.0	2.1523
24	625.1	898.1	1.1135	152.0	2.1818
25	638.2	911.2	1.0975	159.0	2.2014
26	651.7	924.7	1.0814	178.0	2.2504
27	653.0	926.0	1.0798	184.0	2.2648
28	662.5	935.5	1.0689	187.0	2.2718
29	668.7	941.7	1.0619	203.0	2.3075
30	680.4	953.4	1.0489	241.0	2.3820
31	693.9	966.9	1.0342	267.0	2.4265
32	708.5	981.5	1.0188	296.0	2.4713
33	721.4	994.4	1.0056	324.0	2.5105
34	736.9	1009.9	0.9902	366.0	2.5635
35	739.2	1012.2	0.9879	372.0	2.5705
36	744.9	1017.9	0.9824	389.0	2.5899

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
37	752.3	1025.3	0.9753	399.0	2.6010
38	767.0	1040.0	0.9615	473.0	2.6749
39	783.5	1056.5	0.9465	479.0	2.6803
40	792.2	1065.2	0.9388	527.0	2.7218
41	803.4	1076.4	0.9290	552.0	2.7419
42	814.25	1087.25	0.9198	575.0	2.7597
43	826.8	1099.8	0.9093	587.0	2.7686
44	831.0	1104.0	0.9058	598.0	2.7767
45	848.4	1121.4	0.8917	621.0	2.7931
46	869.0	1142.0	0.8756	658.0	2.8182
47	876.3	1149.3	0.8701	702.0	2.8463
48	883.6	1156.6	0.8646	728.0	2.8621
49	897.8	1170.8	0.8541	744.0	2.8716
50	900.0	1173.0	0.8525	759.0	2.8802
51	909.8	1182.8	0.8455	782.0	2.8932
While cooling					
52	904.4	1177.4	0.8493	783.0	2.8937
53	858.0	1131.0	0.8841	677.0	2.8306
54	810.5	1083.5	0.9229	578.0	2.7619
55	781.3	1054.3	0.9485	499.0	2.6981
56	752.0	1025.0	0.9755	418.0	2.6211

VAPOUR PRESSURE DATA OF ZIRCONIUM TETRACHLORIDE OVER THE
RUBIDIUM HEXACHLORO ZIRCONATE (Rb_2ZrCl_6)

Sl. No.	temperature (°C)	temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
1	518.0	791.0	1.2642	32.0	1.5051
2	536.0	809.0	1.2361	36.0	1.5563
3	556.0	829.0	1.2063	40.0	1.6021
4	582.0	855.0	1.1696	44.0	1.6435
5	586.9	859.9	1.1629	48.0	1.6812
6	633.5	906.5	1.1031	50.4	1.7024
7	658.5	931.5	1.0735	82.5	1.9165
8	665.0	938.0	1.0660	87.5	1.9420
9	672.0	945.0	1.0580	89.2	1.9504
10	688.0	961.0	1.0406	101.0	2.0043
11	692.0	965.0	1.0360	109.5	2.0395
12	707.0	980.0	1.0204	124.5	2.0951
13	715.0	988.0	1.0120	151.2	2.1795
14	727.5	1000.5	0.9995	160.1	2.2042
15	731.0	1004.0	0.9960	170.5	2.2317
16	738.0	1011.0	0.9890	195.0	2.2901
17	741.0	1014.0	0.9862	204.4	2.3104
18	757.2	1030.2	0.9707	237.2	2.3751
19	771.9	1044.9	0.9570	248.0	2.3946
20	779.0	1052.0	0.9510	269.7	2.4308
21	784.9	1057.9	0.9453	293.9	2.4683
22	797.0	1070.0	0.9346	346.1	2.5392
23	806.0	1079.0	0.9268	362.0	2.5590
24	818.0	1091.0	0.9166	392.0	2.5933
25	828.0	1101.0	0.9083	412.0	2.6149
26	835.5	1108.5	0.9021	438.0	2.6415
27	846.5	1119.8	0.8930	464.0	2.6665
28	854.8	1127.8	0.8867	492.0	2.6920
29	864.0	1137.0	0.8795	516.0	2.7126
30	872.5	1145.5	0.8730	550.0	2.7404
31	887.2	1160.2	0.8619	590.0	2.7709
32	896.8	1169.8	0.8548	624.0	2.7952
33	904.0	1177.0	0.8496	648.0	2.8116
34	910.9	1183.9	0.8447	670.0	2.8261
35	914.0	1187.0	0.8425	676.0	2.8299
36	918.4	1191.4	0.8393	691.0	2.8395

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
37	922.5	1195.5	0.8365	704.0	2.8476
38	926.0	1199.0	0.8340	714.0	2.8537
39	928.8	1201.8	0.8321	724.0	2.8597
40	931.5	1204.5	0.8302	732.0	2.8645
41	941.0	1214.0	0.8237	761.0	2.8814
While cooling					
42	933.2	1206.2	0.8290	734.0	2.8657
43	898.8	1171.8	0.8534	629.0	2.7987
44	895.0	1168.0	0.8562	628.0	2.7986
45	869.8	1142.8	0.8750	542.0	2.7340
46	847.5	1120.5	0.8925	470.0	2.6721
47	824.2	1097.2	0.9114	407.0	2.6096
48	796.4	1069.4	0.9351	364.0	2.5611

VAPOUR PRESSURE DATA OF HAFNIUM TETRACHLORIDE OVER THE
RUBIDIUM HEXACHLORIDE (Rb_2HfCl_6)

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P (torr)
1	735.4	1008.4	0.9920	66.0	1.8195
2	741.1	1014.1	0.9860	68.0	1.8325
3	743.0	1016.0	0.9840	68.0	1.8325
4	749.0	1022.0	0.9780	69.0	1.8388
5	756.0	1029.0	0.9720	70.0	1.8451
6	764.0	1037.0	0.9640	71.0	1.8513
7	783.5	1056.5	0.9470	74.0	1.8692
8	791.2	1064.2	0.9400	74.0	1.8692
9	805.5	1078.5	0.9270	75.0	1.8751
10	809.0	1082.0	0.9240	76.0	1.8808
11	821.2	1094.2	0.9140	76.0	1.8808
12	825.0	1098.0	0.9110	77.0	1.8865
13	835.5	1108.5	0.9020	78.0	1.8921
14	841.5	1114.5	0.8970	79.0	1.8976
15	843.0	1116.0	0.8960	79.0	1.8976
16	852.0	1125.0	0.8961	80.0	1.9031
17	856.9	1129.9	0.8850	81.0	1.9085
18	860.5	1133.5	0.8822	82.0	1.9138
19	864.5	1137.5	0.8791	82.0	1.9138
20	872.2	1145.2	0.8732	83.0	1.9191
21	875.0	1148.0	0.8711	84.0	1.9243
22	878.0	1151.0	0.8688	85.0	1.9294
23	890.2	1163.2	0.8597	88.0	1.9445
24	901.2	1174.2	0.8516	90.0	1.9542
25	906.5	1179.5	0.8478	91.0	1.9590
26	918.4	1191.4	0.8393	94.0	1.9731
27	923.0	1196.0	0.8361	94.0	1.9731
28	928.0	1201.0	0.8326	96.0	1.9823
29	933.0	1206.0	0.8292	96.0	1.9823
30	940.5	1213.5	0.8241	98.0	1.9912
31	947.3	1220.3	0.8195	100.0	2.0000
32	958.0	1231.0	0.8123	104.0	2.0170
33	965.0	1238.0	0.8078	104.0	2.0170
34	968.5	1241.5	0.8055	108.0	2.0334
35	973.5	1246.5	0.8022	109.0	2.0374
36	979.5	1252.5	0.7984	110.0	2.0414

VAPOUR PRESSURE DATA OF ZIRCONIUM TETRACHLORIDE OVER THE
COMPOUND CESIUM HEXACHLORO ZIRCONATE (Cs_2ZrCl_6)

Sl. No.	temperature (°C)	Temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
1	419.3	692.2	1.4447	17.0	1.2304
2	423.0	696.0	1.4368	17.5	1.2430
3	428.3	701.3	1.4259	18.0	1.2553
4	437.0	710.0	1.4085	19.0	1.2788
5	442.8	715.8	1.3970	19.5	1.2900
6	457.5	730.5	1.3689	21.0	1.3222
7	463.4	736.4	1.3579	21.5	1.3324
8	486.6	759.6	1.3165	24.0	1.3802
9	498.3	771.3	1.2965	25.5	1.4065
10	509.6	782.6	1.2778	27.0	1.4314
11	522.8	795.8	1.2566	29.5	1.4698
12	548.7	821.7	1.2169	31.5	1.4983
13	561.9	834.9	1.1977	35.0	1.5441
14	567.2	840.2	1.1902	35.5	1.5502
15	583.0	856.0	1.1682	37.5	1.5740
16	596.0	869.0	1.1507	42.0	1.6232
17	603.0	876.0	1.1414	42.5	1.6284
18	609.4	882.4	1.1333	43.0	1.6335
19	617.3	890.3	1.1232	44.5	1.6484
20	621.0	894.0	1.1186	45.7	1.6503
21	628.5	901.5	1.1093	54.1	1.7332
22	631.4	904.4	1.1057	64.5	1.8096
23	648.0	921.0	1.0858	55.0	1.7404
24	656.0	929.0	1.0764	56.5	1.7520
25	688.0	961.0	1.0405	79.5	1.9004
26	693.2	966.2	1.0349	83.5	1.9217
27	708.5	981.5	1.0188	88.0	1.9445
28	716.4	989.4	1.0107	103.3	2.0140
29	723.5	996.5	1.0035	106.0	2.0253
30	733.4	1006.4	0.9936	108.3	2.0346
31	746.0	1019.0	0.9813	113.0	2.0531
32	753.5	1026.5	0.9742	117.0	2.0682
33	761.0	1034.0	0.9671	132.0	2.1206
34	778.9	1051.9	0.9507	156.0	2.1931
35	783.0	1056.0	0.9469	161.0	2.2068
36	796.3	1069.3	0.9352	173.2	2.2382

Sl. No.	temperature (°C)	Temperature (°C)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P (torr)
37	811.0	1084.0	0.9225	197.3	2.2949
38	828.7	1101.7	0.9077	210.0	2.3222
39	841.6	1114.6	0.897.2	219.5	2.3414
40	859.5	1132.5	0.8830	244.0	2.3874
41	869.0	1142.0	0.8757	267.0	2.4365
42	873.0	1146.0	0.8726	283.0	2.4518
43	886.4	1159.4	0.8625	295.4	2.4704
44	898.5	1171.5	0.8536	345.0	2.5378
45	922.4	1195.4	0.8365	418.0	2.6212
46	931.8	1204.8	0.8300	441.0	2.6444
47	948.0	1221.0	0.8190	488.0	2.6884
48	963.0	1236.0	0.8091	552.0	2.7419
49	976.5	1249.5	0.8003	592.0	2.7723
50	988.8	1261.8	0.7925	637.4	2.8044
51	997.3	1270.3	0.7872	688.0	2.8376
52	1006.4	1279.4	0.7816	725.3	2.8605
53	1018.8	1291.8	0.7741	753.5	2.8768
54	1027.5	1300.5	0.7689	764.0	2.8831

While cooling

55	980.4	1253.4	0.7978	628.0	2.7979
56	918.0	1191.0	0.8396	433.0	2.6365
57	861.3	1134.3	0.8816	279.0	2.4456
58	831.0	1104.0	0.9058	225.0	2.3522
59	816.5	1089.5	0.9179	207.0	2.3159
60	801.0	1074.0	0.9311	198.0	2.2967

VAPOUR PRESSURE DATA OF HAFNIUM TETRACHLORIDE OVER THE
COMPOUND CESIUM HEXACHLORIDE (Cs₂HfCl₆)

Sl. No.	temperature (°C)	Temperature (°K)	1/T x 10 ³ (°K ⁻¹)	Pressure (torr)	Log P (torr)
1	423.0	696.0	1.4368	11.0	1.0414
2	428.0	701.0	1.4265	11.5	1.0607
3	436.4	709.4	1.4096	12.0	1.0792
4	439.0	712.0	1.4045	12.5	1.0969
5	446.0	719.0	1.3908	12.9	1.1106
6	451.9	724.9	1.3795	13.5	1.1303
7	463.5	736.5	1.3578	14.2	1.1523
8	481.8	754.8	1.3249	17.0	1.2304
9	493.6	766.6	1.3045	19.0	1.2788
10	501.4	774.4	1.2913	19.5	1.2900
11	518.2	791.2	1.2639	22.0	1.3424
12	531.6	804.6	1.2429	23.0	1.3617
13	548.5	821.5	1.2173	24.0	1.3802
14	559.0	832.0	1.2019	25.5	1.4065
15	566.1	839.1	1.1918	26.5	1.4232
16	578.4	851.4	1.1745	27.0	1.4314
17	581.0	854.0	1.1709	27.5	1.4393
18	606.9	879.9	1.1365	31.0	1.4914
19	613.0	886.0	1.1287	32.0	1.5051
20	628.5	901.5	1.1093	33.5	1.5250
21	634.0	907.0	1.1025	34.0	1.5315
22	645.0	918.0	1.0893	35.0	1.5502
23	659.5	932.5	1.0724	40.0	1.6021
24	670.8	943.8	1.0595	43.0	1.6335
25	678.0	951.0	1.0515	44.5	1.6484
26	684.9	957.9	1.0440	49.0	1.6902
27	693.8	966.8	1.0343	54.0	1.7324
28	700.5	973.5	1.0272	57.5	1.7597
29	721.3	994.3	1.0057	66.0	1.8195
30	738.0	1011.0	0.9891	72.5	1.8603
31	752.5	1025.5	0.9751	78.0	1.8921
32	768.7	1041.7	0.9599	83.5	1.9217
33	774.0	1047.0	0.9551	88.0	1.9445
34	798.4	1071.4	0.9333	109.0	2.0374
35	805.8	1078.8	0.9269	111.0	2.0453
36	817.0	1090.0	0.9174	118.0	2.0719

Sl. No.	temperature (°C)	temperature (°K)	$1/T \times 10^3$ (°K ⁻¹)	Pressure (torr)	Log P(torr)
37	836.0	1109.0	0.9017	132.0	2.1206
38	842.4	1115.4	0.8965	136.0	2.1335
39	857.5	1130.5	0.8846	139.0	2.1430
40	866.0	1139.0	0.8779	143.0	2.1553
41	881.0	1154.0	0.8666	164.0	2.2148
42	896.8	1169.8	0.8548	172.0	2.2355
43	907.4	1180.4	0.8472	194.0	2.2878
44	913.0	1186.0	0.8432	203.0	2.3075
45	928.4	1201.4	0.8324	208.0	2.3181
46	936.5	1209.5	0.8268	236.0	2.3729
47	942.0	1215.0	0.8230	248.0	2.3945
48	958.0	1231.0	0.8123	271.0	2.4330
49	967.0	1240.0	0.8065	288.0	2.4594
50	975.4	1248.4	0.8010	301.0	2.4786
51	992.0	1265.0	0.7905	332.0	2.5211
52	1009.3	1282.3	0.7798	362.0	2.5599
53	1016.3	1289.3	0.7756	372.0	2.5705

While cooling

54	985.4	1258.4	0.7947	327.5	2.5152
55	931.0	1204.0	0.8306	228.0	2.3579
56	902.5	1175.5	0.8507	191.0	2.2810
57	884.7	1157.7	0.8638	169.0	2.2279
58	841.0	1114.0	0.8977	137.0	2.1367

APPENDIX - II
EXPERIMENTAL KINETIC DATA

Run No.	Size of NaCl particle, d_o , (mm)	Time (hours)	W Initial weight of NaCl (g)	W' Weight gain by NaCl (g)	Weight loss by $ZrCl_4$ (g)	Fraction reacted, $F = \frac{W'}{W} (0.5016)$ $\times 10^4$	P_{ZrCl_4} (atm) $\times 10^3$	P_{ZrCl_4} mm, Hg	J = $(1-(1-F)^{1/3})^2 \times 10^6$
K13	2.88605	12.08	1.4589	0.0185	7.1104	62.09	5.12	3.3889	4.3
K19		18.20	1.2944	0.0312	12.6216	121.01	6.03	4.58	16.4
K8		23.00	1.0592	0.0304	16.6613	144.12	6.29	4.79	23.3
K16		30.00	1.2416	0.0398	19.8431	160.68	5.75	4.37	29.0
K1	2.0484	06.00	2.2861	0.0282	2.0804	61.94	3.02	2.29	4.28
K2		15.08	3.1582	0.0736	5.2312	116.90	3.02	2.29	15.3
K5		33.33	4.0631	0.1605	11.4502	198.10	2.99	2.28	44.2
K14	1.4476	12.08	0.9335	0.0369	7.1104	198.12	5.12	3.89	44.2
K20		18.20	1.1176	0.0547	12.6216	245.70	6.03	4.58	68.2
K17		30.00	1.0083	0.0646	19.8431	321.19	5.75	4.37	117.1
K15	0.86354	12.08	1.0445	0.1074	7.1104	515.84	5.13	3.89	306.2
K21		18.20	0.9321	0.1233	12.6216	663.80	6.03	4.58	512.3
K18		30.00	0.8845	0.1408	19.8431	798.47	5.75	4.37	748.4